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List of Physico-chemical Symbols adopted by the Chemical Society.

[See J.C.S., 1921, **119**, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation.....	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity.....	g	
Mechanical equivalent of heat	J	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height.....	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c t_c, T_c d_c	
Reduced quantities: pressure, volume, temperature, density	p_r, v_r t_r, T_r, d_r	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	σ
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	K, (K_c, K_p)	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal,		

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

Wave-length of light	λ	
Refractive index	n	n_r
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]^t_\lambda$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]^t_\lambda$	
Molecular refractive power	R_G, R_L $[R_G]^t_\lambda$, $[R_L]^t_\lambda$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10}, Λ_v, Λ_∞	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions	Λ_K, Λ_{Cl}	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
δ	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h$, ${}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	Gas constant per mole; electrical resistance.
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_{cs}	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_{cs}	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_c, v_r	Critical volume : reduced volume.
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
${}_0\epsilon_h, {}_0\epsilon$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
$\Lambda_{10}, \Lambda_v, \Lambda_\infty$	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

CXCVII.—*The Inter-relationships of the Sulphur Acids.*

By Henry Bassett and Reginald Graham Durrant.

This investigation arose out of an attempt to explain the genesis of polythionates in the Wackenroder reaction and in the decomposition of thiosulphates by acid. It soon became clear that the reactions of many of the sulphur acids required further study before the formation of polythionic acids could be understood.

In all the reactions of the sulphur acids, the hydrogen-ion concentration plays a very important part and in great measure determines the path followed. Addition of acid, *i.e.*, hydrogen ions, to a system should, in accordance with the principle of Le Chatelier, favour reactions which remove hydrogen ions, whilst hydroxyl ions should produce exactly the opposite effect. These deductions are, on the whole, borne out by experiment.

The method adopted in the theoretical portion of the present paper is to consider all reactions and give all equations in terms of the acids concerned, even although the reactions may occur in alkaline solutions. This has been done for the sake of simplicity and uniform treatment, and must not be taken to mean that the reactions may not follow an ionic course, although we think it probable that many of the reactions discussed do actually involve the non-ionised acids rather than their ions.

A number of equations have to be referred to frequently. These are given in the text in the positions where they are first considered. To each has been given a number by which it is referred to on subsequent occasions, and for convenience in reference all such equations are here collected in the order of their first appearance, equations mentioned only once not being included; *a* after the number of an equation signifies the reaction from left to right, *b* that from right to left.

$$2S + 2H_2O \rightleftharpoons H_2S + (HO)_2S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

$$S(OH)_2 + HO{\cdot}S{\cdot}O{\cdot}S{\cdot}OH \rightleftharpoons H_2S + H_2S_2O_5 \quad . \quad . \quad . \quad . \quad (II)$$

$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH \rightleftharpoons (HO)_2S{\cdot}SO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH + H_2O \rightleftharpoons S(OH)_2 + \begin{matrix} H_2O + SO_2 \\ \uparrow\downarrow \\ H_2SO_3 \end{matrix} \quad . \quad . \quad . \quad . \quad (IV)$$

$$S(OH)_2 + SO_2 \rightleftharpoons (HO)_2S{\cdot}SO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH + (HO)_2S{\cdot}SO_2 \rightleftharpoons H_2S_2O_5 + H_2S_2O_3 \quad . \quad . \quad (VI)$$

$$H_2SO_3 + H_2S_2O_5 \rightleftharpoons H_2SO_4 + H_2S_2O_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (VII)$$

$$H_2S_2O_3 \rightleftharpoons H_2SO_3 + S \; (2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2) \quad . \quad . \quad (VIII)$$

$$2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IX)$$

$$2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (X)$$

$$H_2S_2O_7 + H_2S \rightleftharpoons H_2S_3O_6 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (XI)$$
$$H_2S_3O_6 + S \rightleftharpoons H_2S_4O_6 \; (2H_2S_3O_6 + S_2 \rightleftharpoons 2H_2S_4O_6) \quad . \quad (XII)$$
$$H_2S_4O_6 + S \rightleftharpoons H_2S_5O_6 \; (2H_2S_4O_6 + S_2 \rightleftharpoons 2H_2S_5O_6) \quad . \quad (XIII)$$
$$H_2S_3O_6 + H_2S_2O_3 \rightleftharpoons H_2S_4O_6 + H_2SO_3 \quad . \quad . \quad . \quad . \quad . \quad (XIV)$$
$$H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3 \quad . \quad . \quad . \quad . \quad . \quad (XV)$$

In order to save space and avoid repetition, the experimental portion of the paper contains only the practical details of experiments, their connexion with the theoretical discussion being indicated by cross references. Any purely qualitative experiments which are discussed in the theoretical part are not, as a rule, referred to again in the experimental part.

The Hydrolysis of Sulphur. Sulphoxylic Acid.

It has been generally supposed that hydrogen sulphide and sulphurous acid are the first products of the hydrolysis of sulphur (Cross and Higgin, J., 1879, **35**, 249; *Ber.*, 1883, **16**, 1195) and may give rise to thiosulphuric or other sulphur acids.

This view is probably incorrect, for, just as the hydrolysis of chlorine results in the production of equivalent amounts of hydrogen chloride and hypochlorous acid, so the hydrolysis of sulphur should give equivalent amounts of hydrogen sulphide and sulphoxylic acid, $(HO)_2S$. The latter is doubtless a very unstable substance and would readily undergo further change.

Although neither free sulphoxylic acid nor its salts are known, there are two simple derivatives which are readily accessible. These are sodium formaldehydesulphoxylate and sodium hydrosulphite [hyposulphite]. We have shown that when sulphoxylic acid is liberated from the formaldehyde compound by hydrolysis it undergoes decomposition into hydrogen sulphide and sulphurous acid—a change analogous to that undergone by hypochlorous acid. If the hydrolysis occurs in presence of a lead, arsenic, antimony, stannous, bismuth, cadmium, nickel, cobalt, or zinc salt, the sulphide of the metal is precipitated. No acid, other than that present in the solution owing to hydrolysis, must be added in the case of zinc, nickel, or cobalt, otherwise the precipitate of sulphide fails to appear; and very little must be present in the case of cadmium. With salts of silver, copper, and mercury, reduction to metal occurs. This may occur also with arsenic and probably with antimony or bismuth, especially in absence of much acid, whilst, conversely, a little sulphide may be formed in the case of copper and silver in presence of much acid. Precisely what happens in such cases depends upon the relative rates of the oxidation of sulphoxylic acid to sulphurous acid or of its change into hydrogen

sulphide and sulphurous acid. These rates are affected by concentration of reactants, acidity, and temperature (compare results with sodium hydrosulphite, $Na_2S_2O_4$, Firth and Higson, J., 1923, **123**, 1515; *J. Soc. Chem. Ind.*, 1923, **42**, 427T).

In absence of salts of heavy metals, the hydrogen sulphide acts upon the formaldehyde to some extent to yield trithioformaldehyde, which appears as white crystals or oily drops and is readily detected by its characteristic smell. The normal interaction of hydrogen sulphide and sulphurous acid leads to formation of sulphur and polythionic acids (see Expt. D).

On alkaline hydrolysis sulphur gives rise to polysulphide and thiosulphate (Gmelin, "Handbook of Chemistry," Watts's English Transl., 1849, II, 160; Auld, J., 1915, **107**, 480), both of which could result from further action of sulphur on previously formed sulphide and sulphite.

The acid hydrolysis of the formaldehydesulphoxylate occurs rapidly on heating, but is slow at the ordinary temperature; the actual rate depends also upon the acidity. The alkaline hydrolysis is extremely slow, but seems to follow a similar course to the acid hydrolysis, yielding sulphide and sulphite.

The action of formaldehydesulphoxylate on sodium plumbite solutions is slow at the ordinary temperature, but more rapid on heating. A mixture of metallic lead and lead sulphide is usually formed, a high concentration of sulphoxylate and high alkalinity being most favourable to the precipitation of lead sulphide. The reduction to metallic lead is due to the sulphoxylate, and not to the formaldehyde (Expt. A). In presence of plumbite, it is the formation of insoluble lead sulphide which accelerates the hydrolysis of the formaldehydesulphoxylate. Sulphur will produce a similar effect by converting the sulphite, formed on hydrolysis of the sulphoxylate, into thiosulphate. Thus it was found that, after an alkaline solution of formaldehydesulphoxylate had been boiled with sulphur and the polysulphide (much of which was, of course, due to alkaline hydrolysis of the sulphur) removed with lead acetate, the solution was no longer capable of bleaching methylene-blue. A similar alkaline sulphoxylate solution, after being boiled for the same length of time without sulphur, gave no precipitate with lead acetate and still had a strong bleaching action on methylene-blue (see also p. 1424). On boiling an alkaline solution of sodium hydrosulphite to which sodium plumbite has been added, a greyish-black precipitate of lead sulphide and metallic lead is obtained. The same reaction occurs at the ordinary temperature, but much more slowly. If the alkaline hydrosulphite solution is boiled and then cooled to room temperature before the sodium plumbite is added,

an immediate black precipitate appears which consists of pure lead sulphide if only small quantities of hydrosulphite and plumbite are used in the experiment.

The work of Binz (*Ber.*, 1904, **37**, 3549), Bazlen (*Ber.*, 1905, **38**, 1067), and Reinking, Dehnel, and Labhardt (*ibid.*, p. 1069) leaves little doubt that sodium hydrosulphite, $Na_2S_2O_4$, is to be considered as the sodium salt of a mixed anhydro-acid derived from one molecule of sulphoxylic acid and one of sulphurous acid. At the ordinary temperature, it is so stable towards alkali that sodium hydroxide can be used to salt it out from its aqueous solution (Bernthsen and Bazlen, *Ber.*, 1900, **33**, 126). Bazlen (*loc. cit.*, p. 1057) showed that both before and after such salting-out the hydrosulphite had the formula $Na_2S_2O_4,2H_2O$. The experiments with lead, which have just been described, show that the hydrosulphite is hydrolysed slowly in alkaline solution even at the ordinary temperature, and the reactions then observed are the same as those obtained with sodium formaldehydesulphoxylate—both being the reactions of sulphoxylic acid or its decomposition products. If the solution is boiled before the plumbite is added, a precipitate of lead sulphide free from metallic lead can be obtained in the case of the hydrosulphite, because the sulphoxylate is converted into sulphide and sulphite as fast as it is formed. If the plumbite is present during the liberation of the sulphoxylate, some of the latter is oxidised by the plumbite before it is converted into sulphide and sulphite, and so a mixture of lead sulphide and lead is obtained. Alkaline solutions of sulphite give no reaction with plumbite under the conditions of these experiments, whilst thiosulphate in alkaline solution gives a very faint reaction which will be discussed in a later section (p. 1418).

The readiness with which sulphoxylic acid is converted into hydrogen sulphide and sulphurous acid in acid solution, or into sulphide and sulphite in alkaline solution, is quite sufficient to explain why hydrogen sulphide and sulphurous acid have been held to be the first products of the hydrolysis of sulphur. In view of these results, however, it is felt that there is every justification for considering that the primary reaction in the hydrolysis of sulphur, whether this occurs in acid or in alkaline solution, is correctly represented by the equation

$$2S + 2H_2O \rightleftharpoons H_2S + (HO)_2S \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Attempts to verify this equation directly have not been successful, but they do not disprove it.

The action of moist sulphur on silver and other metals, even at the ordinary temperature, is undoubtedly due to slow hydrolysis of

the sulphur, which is accelerated by removal of the hydrogen sulphide as insoluble sulphide of the metal. Similarly, solutions of silver salts, or salts of other metals which form very sparingly soluble sulphides, are readily acted upon by sulphur on boiling. A quantitative experiment in which sulphur was digested with metallic silver in presence of chromic acid was in better agreement with reaction (I) than with a reaction $3S + 3H_2O \rightleftharpoons 2H_2S + H_2SO_3$, since approximately one molecule each of silver sulphide and sulphuric acid were formed (Expt. B).

When finely-ground rhombic sulphur was boiled with silver acetate solution, the alteration of the sulphur was very superficial owing to the dense, coherent film with which it became covered. This so effectively protected the sulphur that it was impossible to remove it completely even by long-continued extraction in a Soxhlet apparatus with benzene or carbon disulphide. Whether the film consisted of a mixture of silver sulphide and silver in the proportion to be expected from equation (I), could not therefore be determined.

The reactions $2S(OH)_2 = H_2S + H_2SO_4$ and $2S(OH)_2 = H_2S_2O_3 + H_2O$ look simple, but we can find no evidence that either of them occurs, although we have a certain amount of negative evidence against them. If sulphoxylic acid could undergo either of these changes, alkali should promote the changes, since both would correspond to a considerable increase in hydrogen ion. We find, however, that there is no sulphate produced when sodium formaldehydesulphoxylate is boiled with alkaline plumbite solution (Expt. C). Neither is any sulphate produced when sodium formaldehydesulphoxylate is hydrolysed in acid solution either alone or in presence of lead or arsenious salts (Expt. D). If the arsenious sulphide formed had resulted from the decomposition of thiosulphate, large amounts of sulphate would have been formed, as special experiments showed (Expt. E).

Long heating of alkaline solutions of sodium formaldehydesulphoxylate did not seem to lead to the formation of any thiosulphate; the sulphoxylate was apparently unchanged.

Sulphur separates at once when a strong hydrosulphite solution is added to concentrated hydrochloric acid, whereas when sodium thiosulphate is so added no separation of sulphur occurs for a long time (see p. 1430). If the sulphoxylic acid formed on hydrolysis of the hydrosulphite changed rapidly into thiosulphate, no separation of sulphur would therefore have been expected. That it does separate is not due to the presence of sulphite, for a solution containing an equimolecular mixture of sodium metabisulphite and thiosulphate did not yield any sulphur on being added to concentrated hydrochloric acid, except after long standing.

Foerster, Lange, Drossbach, and Seidel (*Z. anorg. Chem.*, 1923, **128**, 268) assume that the reaction $2S(OH)_2 = H_2S_2O_3 + H_2O$ does occur, and at one time we thought the same, but we have reached the conclusion that there is no justification or need for the assumption. At first sight such a change seems to be indicated by the fact that sodium hydrosulphite, in absence of air, in neutral or faintly acid solutions, changes quantitatively into sulphite and thiosulphate (Meyer, *Z. anorg. Chem.*, 1903, **34**, 43; K. Jellinek and E. Jellinek, *Z. physikal. Chem.*, 1919, **93**, 325). The solid salt undergoes a similar change, and old specimens contain large amounts of thiosulphate. It is probable that in this change the thiosulphate is not formed directly from sulphoxylic acid, but by a more complex mechanism which is considered on p. 1411.

The mechanism of the change of sulphoxylic acid into hydrogen sulphide and sulphurous acid calls for comment. A reaction $3S(OH)_2 \rightleftharpoons H_2S + 2H_2SO_3$ seems improbable because (i) it would be termolecular although it actually occurs very readily, and (ii) it is more likely that dissimilar molecules are respectively oxidised and reduced. We suggest that it is sulphoxylic acid itself which is reduced, whilst its anhydro-acid, HO·S·O·S·OH, which is isomeric with thiosulphuric acid, is oxidised. This would give a reaction represented by the equation

$$S(OH)_2 + HO{\cdot}S{\cdot}O{\cdot}S{\cdot}OH \rightleftharpoons H_2S + H_2S_2O_5 \quad . \quad . \quad (II),$$

where the $H_2S_2O_5$ is pyrosulphurous acid. The reversal of this change would be the first step in the Wackenroder reaction (see p. 1440)

The position with regard to equilibrium (II), as disclosed by the reactions of formaldehydesulphoxylate with metallic salts, is somewhat peculiar. On the one hand, with arsenious chloride, increase in *acidity* favours precipitation of arsenious sulphide instead of elementary arsenic, which is formed when little free acid is present, but, on the other hand, in presence of sodium plumbite, increase in *alkalinity* favours formation of lead sulphide, the proportion of metallic lead which is precipitated increasing as the alkalinity decreases. These two results, although at first sight contradictory, can be explained on the basis of equation (II). The reaction would proceed from left to right with a considerable increase in hydrogen ions, for there can be little doubt that sulphoxylic acid would be a very weak acid just as hypochlorous acid is. Alkali should therefore favour the change into sulphide and sulphite, which agrees with the results of the plumbite experiments. In acid solution, high acidity might be expected to favour formation of anhydrosulphoxylic acid at the expense of sulphoxylic acid, and this also would accelerate the change of the latter into hydrogen sulphide

and pyrosulphite. The effect of high acidity in favouring precipitation of arsenious sulphide, rather than of free arsenic, would then be intelligible. Increase in acidity would also tend to produce sulphur dioxide at the expense of either sulphurous or pyrosulphurous acid, and this also would hasten the decomposition of sulphoxylic acid. Reaction (I *b*) occurs with decrease of hydrogen ions, and so will be favoured by acidic conditions. It is this interaction of hydrogen sulphide and sulphoxylic acid which leads to the decomposition of sulphoxylic acid in acid solution in absence of metals which form insoluble sulphides. Such decomposition could be represented by the summation equation

$$2S(OH)_2 \rightleftharpoons H_2SO_3 + S + H_2O.$$

To postulate the existence of an anhydro-compound, such as HO·S·O·S·OH, under alkaline conditions may be considered unreasonable. This objection has been raised by Bucherer and Schwalbe (*Ber.*, 1906, **39**, 2814) to the unsymmetrical formula for sodium hydrosulphite. However, sulphoxylic acid may be expected to be a very weak acid, and anhydro- (or pyro-) or even meta-salts of weak acids can certainly exist in alkaline solution; for instance, the borates $Na_2B_2O_4,4H_2O$ and $K_2B_2O_4,2\frac{1}{2}H_2O$ can separate from solutions containing a large excess of alkali (Dukelski, *Z. anorg. Chem.*, 1906, **50**, 41).

Vogel and Partington (J., 1925, **127**, 1522) claim to have prepared solid, crystalline sodium sulphoxylate, Na_2SO_2, and sodium ethyl sulphoxylate, $NaEtSO_2$. The sodium sulphoxylate is said to be practically unattacked by boiling concentrated hydrochloric or sulphuric acid, although attacked by a hot mixture of fuming nitric acid and bromine. Such behaviour is most improbable, and our view is that these authors were actually dealing with more or less impure sodium sulphate. In any case it is certain that sodium sulphate is precipitated on addition of sulphuric acid to a solution of sodium compounds in absolute alcohol, and such addition was an important step in the recorded preparations.

Hydrosulphurous Acid.

The Factors which determine Colour in Simple Sulphur Compounds.—On the whole, the term "hydrosulphite," which is in fairly general use, would seem to be as good as any which has been suggested for the salt $Na_2S_2O_4$. "Hyposulphite," the official term, does not seem satisfactory, partly because this name has become so firmly attached to what is more correctly called thiosulphate, and partly because it is doubtful whether one could correctly apply it to $Na_2S_2O_4$, even if this complication did not exist. We

consider that it is sulphoxylic acid, $S(OH)_2$ or H_2SO_2, which alone has any right to be called hyposulphurous acid. Since $H_2S_2O_4$ is a "mixed" anhydro-acid, it has no right to the name, as it does not belong to the simple sulphuric–sulphurous series at all, any more than thiosulphuric acid does.

We cannot discuss all the evidence for the unsymmetrical anhydro-acid structure of the hydrosulphites, but merely wish to direct attention to the fact that the action of various oxidising agents strongly indicates this structure. Mild oxidising agents, such as silver salts, normally oxidise hydrosulphite to sulphite, but the action of molecular oxygen is exceptional, for Meyer (*loc. cit.*) showed that in this case sulphite and sulphate are formed. His figures indicate that these would be in equimolecular proportion were it not for disturbances due to hydrolysis of hydrosulphite by the acid formed as the oxidation proceeds. This seems to agree particularly well with the unsymmetrical formula. We have found that, in solutions containing sufficient sodium carbonate to neutralise the acid as it is formed, the atmospheric oxidation of hydrosulphite proceeds smoothly as a unimolecular reaction (Expt. F).

Solutions of sodium hydrosulphite, as is well known, become yellowish-brown on acidification. With concentrated solutions, the colour may be as deep as, and very similar to, that of $N/10$-iodine. The smell of hydrogen sulphide is quite evident directly after acidification, but is soon masked by that of sulphur dioxide. This formation of hydrogen sulphide is not generally mentioned, and although Bernthsen (*Annalen*, 1881, **208**, 172) and Meyer (*loc. cit.*) mention that cadmium sulphide is precipitated when hydrosulphite solutions containing cadmium sulphate are acidified, they do not appear to have noticed the hydrogen sulphide itself. Sulphur eventually separates from the acidified solution, but the time which elapses before this occurs may be considerable. The colour persists longest when the acidification has been effected by sulphurous acid. If a strong sodium hydrosulphite solution is added to concentrated hydrochloric acid, one obtains but a momentary brown colour, and a precipitate of sodium chloride and sulphur separates at once.

The colour of acid hydrosulphite solutions has never been satisfactorily explained. It has usually been regarded as the colour of the free acid, but, according to present-day views, since the salts are colourless the acid should be colourless too, unless some change of constitution occurs after it is set free from its salts. The bright, clear, deep-coloured solutions do not at all give the impression of colloidal solutions of sulphur, a possibility which has been mooted (Abegg's Handbuch, 1908, II, Pt. 1, p. 262).

When considering a possible explanation of the colour, several other instances of colour in simple sulphur compounds or their solutions should be borne in mind. The chief of these are : (1) Sulphur itself—the much deeper colour of plastic sulphur as compared with crystalline sulphur is of interest. (2) Sulphur mono- and di-chlorides, which are yellow. (3) Sulphur tetrachloride, which has a brownish-red colour. (4) The polysulphides. (5) The yellow or greenish-yellow solutions obtained by saturating strong alkali-metal or ammonium bisulphite solutions with sulphur dioxide. (6) The yellow solutions obtained by the action of sulphur dioxide on thiosulphate solutions : yellow solids, $K_2S_2O_3,SO_2$ and $Rb_2S_2O_3,SO_2$ have recently been prepared by Foerster and Vogel (*Z. anorg. Chem.*, 1926, **155**, 161). (7) The yellow compounds of sulphur dioxide with potassium thiocyanate and with potassium iodide (Fox, *Z. physikal. Chem.*, 1902, **41**, 458; Ephraim and Kornblum, *Ber.*, 1916, **49**, 2007).

Since potassium bromide and chloride combine with sulphur dioxide to form colourless compounds, it would appear that the colour of the potassium iodide compounds is in some way due to the iodine. The potassium iodide–sulphur dioxide compound need not therefore be considered in the present connexion. The compound $KCNS,SO_2$ would, however, seem to owe its colour in some way to the attachment of sulphur dioxide to the sulphur of the thiocyanate.

According to the modern theories of valency, the sulphur atom in all its ordinary compounds is surrounded by an outer shell of 8 electrons. This is true of all the sulphur atoms in the following, among others : The S″ ion of the sulphides, the HS′ ion, hydrogen sulphide, sulphites, sulphates, thiosulphates, and polythionates. The co-ordination number of these substances ranges from zero in the case of the S″ ion to 4 in the case of the sulphates. Nevertheless, all these compounds (unless a colour-giving positive ion is present) are colourless. The lack of visible colour seems, then, to depend upon the one common characteristic, the shell of 8 electrons, and is evidently independent of the state of the atom with respect to co-ordination.

The existence of the very stable sulphur hexafluoride shows that sulphur in suitable combination can have as many as 12 electrons in its outer shell. This compound also is colourless.

In sulphur tetrachloride, the sulphur atom would have an outer shell of 10 electrons, and since this compound has a brownish-red colour, it may well be that it is essentially the 10-electron sheath which determines visible colour in all the compounds we are considering. In potassium thiocyanate, the sulphur atom has the

normal 8-electron sheath, but when it becomes co-ordinated with a molecule of sulphur dioxide in the compound $KCNS,SO_2$, it is then surrounded by a 10-electron sheath, and the compound is yellow.

Most of the other yellow sulphur compounds referred to above can be accounted for on this basis. The greenish-yellow sulphite solutions owe their colour to H_2SO_3,SO_2—perhaps better written as $H_2\left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\SO_2\end{matrix}\right]$, which is isomeric with pyrosulphurous acid, $H_2\left[\begin{matrix}O\\O\end{matrix}SOS\begin{matrix}O\\O\end{matrix}\right]$. The yellow colour of thiosulphate solutions which have been treated with sulphur dioxide would be due to $H_2\left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\S\cdot SO_2\end{matrix}\right]$. In both these cases the sulphur atom to which the sulphur dioxide becomes attached would have a 10-electron sheath.

When hydrosulphurous acid is liberated from its salts, it will be readily hydrolysed to sulphoxylic acid and sulphurous acid. The yellowish-brown colour is most probably due to a compound, $(HO)_2S\cdot SO_2$, obtained by the co-ordination of one molecule of sulphur dioxide with the sulphur atom of a molecule of sulphoxylic acid. It could also arise directly by a simple intramolecular change. This compound is isomeric with hydrosulphurous acid itself, which may be written HO·S·O·SO·OH. When sulphur dioxide is passed into a solution of sodium formaldehydesulphoxylate, a solution of precisely the same colour is obtained as from sodium hydrosulphite. The properties of the two solutions are similar, and the coloured compound may be the same in the two cases. It is possible, however, that the formaldehyde still remains attached in the one case.

It is noteworthy that formaldehyde removes the colour from solutions of all the above sulphur dioxide addition compounds owing to formation of the very stable formaldehydesulphurous acid.

Sulphur monochloride, S_2Cl_2, would be expected on the above theory to be colourless. Its yellow colour may possibly be due to association in the liquid state, *i.e.*, co-ordination of one molecule with the sulphur atoms of other molecules.

The colour of sulphur itself and of the polysulphides is explicable on the basis of a colourless $S<\begin{matrix}S\\S\end{matrix}$ molecule, with a structure similar to that assigned by Rankine (*Proc. Physical Soc.*, 1922, 35, 33) to sulphur dioxide, in which all three sulphur atoms have 8-electron sheaths, or of an S_3 molecule of structure S=S—S, in which each sulphur atom would also have an 8-electron sheath. In hydrogen trisulphide, which is yellow, one of the sulphur atoms would have a 10-electron sheath, and so on. Hydrogen disulphide, which is

presumably H·S·S·H, is colourless (Walton and Parsons, *J. Amer. Chem. Soc.*, 1921, **43**, 2539).

Sulphur tetrachloride is the only coloured sulphur compound which has been considered that does not contain sulphur–sulphur linkages, but it seems unlikely that such linkages in themselves have any great influence on the colour, since thiosulphates, polythionates, etc., in which such linkages occur, are colourless. The 10-electron sheath seems to be the important factor, although, of course, the actual colour of any particular compound must depend to some extent upon its structure and composition as a whole. It may well be that union of 10-electron sulphur with 8-electron sulphur promotes colour in a similar way to that assumed by Willstätter and Piccard (*Ber.*, 1908, **41**, 1465) in organic compounds with a *meri*-quinonoid structure.

The decomposition of hydrosulphurous acid can be briefly summed up thus:

$$HO\cdot S\cdot O\cdot SO\cdot OH \rightleftharpoons (HO)_2S\cdot SO_2 \quad . \quad . \quad . \quad . \quad \text{(III)}$$

$$HO\cdot S\cdot O\cdot SO\cdot OH + H_2O \rightleftharpoons S(OH)_2 + \begin{matrix} H_2O + SO_2 \\ \uparrow\downarrow \\ H_2SO_3 \end{matrix} \quad . \quad . \quad \text{(IV)}$$

$$S(OH)_2 + SO_2 \rightleftharpoons (HO)_2S\cdot SO_2 \quad . \quad . \quad . \quad . \quad \text{(V)}$$

Whether direct rearrangement of the two isomeric forms of $H_2S_2O_4$ occurs, or whether one form is converted into the other *via* sulphoxylic acid formed by hydrolysis, it is not possible to say. Very likely both methods of change occur.

Since two sulphur atoms are directly united in $(HO)_2S\cdot SO_2$, its ready reduction to thiosulphate might be anticipated. K. Jellinek and E. Jellinek (*loc. cit.*) showed that hydrosulphurous and thiosulphuric acids are successive stages in the electrolytic reduction of sulphurous acid. Oxidation of $HO\cdot S\cdot O\cdot SO\cdot OH$ by $(HO)_2S\cdot SO_2$ probably accounts for the change of hydrosulphite into thiosulphate and pyrosulphite in accordance with the equation:

$$HO\cdot S\cdot O\cdot SO\cdot OH + (HO)_2S\cdot SO_2 \rightleftharpoons H_2S_2O_5 + H_2S_2O_3 \quad . \quad \text{(VI)}$$

The change follows a bimolecular course (K. Jellinek and E. Jellinek, *loc. cit.*). The Jellineks' observation, that in presence of sodium bisulphite the rate of change is greater and roughly proportional to the square of the bisulphite concentration, is probably due to a stabilising effect of the sulphite on the two forms of hydrosulphurous acid in accordance with reactions (IV) and (V).

In acid hydrosulphite solutions there occur, superimposed on the above changes, the two reactions of sulphoxylic acid represented by equations (I) and (II). In addition, there is the possibility of polythionic acid formation, either by interaction of hydrogen

sulphide and sulphurous acid or by decomposition of thiosulphate (see pp. 1416—17 and 1440). Polythionates appear to be always formed during the decomposition of hydrosulphurous acid (Foerster, Lange, Drossbach, and Seidel, *loc. cit.*, p. 278).

The fairly permanent, yellow colour, which remains after the yellowish-brown colour of $(HO)_2S{\cdot}SO_2$ has disappeared, is due to the sulphur dioxide–thiosulphuric acid complex.

Freshly acidified hydrosulphite has a most unpleasant smell suggestive of, but differing from, that of hydrogen sulphide, and not like a mixture of hydrogen sulphide and sulphur dioxide. It reminds one of sewer gas more than anything else, and it may well be the smell of sulphoxylic acid.

The Autoxidation of Sulphurous Acid.

It is known that in absence of air solutions of sulphurous acid slowly undergo a change which is generally represented by the equation $3H_2SO_3 = 2H_2SO_4 + S + H_2O$. This change is greatly accelerated by a high temperature or exposure to light.

Foerster, Lange, Drossbach, and Seidel (*loc. cit.*) have recently made a careful and exhaustive study of this reaction. With some of the theoretical conclusions of these authors we cannot agree, and we shall briefly explain our own views without adducing full details of the evidence. We agree with them (*loc. cit.*, p. 267) that two different molecules must be concerned in the oxidation and reduction which is the first step in the autoxidation, but not with their suggestion that these are two different forms of the HSO_3' or S_2O_5'' ions reacting according to the equations: $2HSO_3' \longrightarrow SO_4'' + H_2SO_2$; $S_2O_5'' \longrightarrow SO_4'' + SO$, where H_2SO_2 is sulphoxylic acid and SO its anhydride.

We consider that the reaction

$$H_2SO_3 + H_2S_2O_5 \rightleftharpoons H_2SO_4 + H_2S_2O_4 \quad . \quad . \quad . \quad \text{(VII)}$$

is far more probable, this equation being regarded as applying to the reactions of the respective ions as well as to the non-ionised acids, as mentioned on p. 1401. We have already (p. 1406) given reasons for the view that pyrosulphurous acid is the oxidising agent in the Wackenroder reaction, and if so, it is probably the oxidising agent in the autoxidation reaction also. Solutions of sulphurous acid appear to contain most of their sulphur dioxide as such (Wright, J., 1914, **105**, 2907), whilst solutions of alkali-metal bisulphites contain some pyrosulphite (metabisulphite) (Baly and Bailey, J., 1922, **121**, 1813; Getman, *J. Physical Chem.*, 1926, **30**, 266). It is not unreasonable to suppose that there is some pyrosulphurous acid even in "sulphurous acid" solutions. Since sulphate appears

from the very beginning of oxidation, sulphurous acid is probably the substance oxidised. $H_2S_2O_4$, hydrosulphurous acid, is then the most probable product of reduction of the pyrosulphurous acid.

Since the hydrosulphurous acid is unstable under the prevailing conditions, it does not accumulate but rapidly undergoes further change (p. 1411). This makes the proof of its formation difficult.

Jungfleisch and Brunel (*Compt. rend.*, 1913, **156**, 1719) stated that they had obtained all the reactions for hydrosulphite at the stage of the autoxidation just prior to the separation of sulphur. Foerster and his colleagues (*loc. cit.*, pp. 277, 288, 293, and 300) could only partly confirm this, although they admitted that in some cases small quantities of hydrosulphite are formed at some stage of the reaction.

The only reaction for hydrosulphite which can be obtained in these sulphite solutions undergoing autoxidation is the bleaching of indigo, which is very delicate (but see p. 1439).

Sulphur dioxide co-ordinated with thiosulphate or iodide [$H_2S_2O_3{\cdot}(SO_2)_x$; $HI(SO_2)_x$] may also be able to oxidise sulphurous acid and perhaps more rapidly than does pyrosulphurous acid. This would be represented by $H_2SO_3 + [SO_2] = H_2SO_4 + [SO]$, where square brackets indicate a co-ordinated condition; such a reaction could account for the remarkable way in which iodide or thiosulphate accelerates autoxidation of sulphurous acid (Foerster *et al.*, *loc. cit.*, pp. 266—269).

If our views expressed on pp. 1409—10 are correct, the yellow bisulphite solutions contain $H_2SO_3{,}SO_2$, in which the sulphur dioxide is co-ordinated in a similar way to that present in the iodide and thiosulphate complexes. The colour and other indications suggest that this form of pyrosulphurous acid is practically absent from sulphurous acid solutions, especially weak ones, which nevertheless undergo slow autoxidation. It seems likely, therefore, that it is the colourless pyro-acid form of $H_2S_2O_5$ (corresponding to the solid, colourless pyrosulphites or metabisulphites) —$SO_2H{\cdot}O{\cdot}SO_2H$— which is normally responsible for the first step in the autoxidation of sulphurous acid solutions (reaction VII), and that it is the pyro-acid form of hydrosulphurous acid —$H{\cdot}SO_2{\cdot}O{\cdot}S{\cdot}OH$— which is produced in this first step.

Some of the pyro-acid form of hydrosulphurous acid undergoes rearrangement to the coloured form, $H_2SO_2{\cdot}SO_2$, and the two forms then react to yield thiosulphate and pyrosulphite (reaction VI).

The middle phase of the autoxidation of sulphurous acid is essentially the decomposition of thiosulphuric acid (discussed on pp. 1416—40). Trithionic acid, one of the first products of this decomposition, gradually yields tetra- and penta-thionic acids as

the concentration of sulphurous acid diminishes with the progress of the autoxidation. The polythionic acids finally decompose in their turn, and the final products of the autoxidation are sulphur and sulphuric acid.

On account of this polythionic acid formation during autoxidation, tri- and tetra-thionic acids are almost always present in old sulphurous acid solutions, whether these have been entirely protected from atmospheric oxidation or not. As the thionic acids are slowly decomposed in acid solution, the amount surviving in any given case depends upon the age and composition of the solution (Expt. G, Table I).

No separation of sulphur occurs for a long time, because the excess of sulphurous acid stabilises both the sulphoxylic and the thiosulphuric acids by yielding with them the sulphur dioxide addition complexes. Formation of thiosulphate from sulphite and sulphur, according to reaction (VIII), is greatly facilitated, and also the formation of trithionate in accordance with reaction (IX), the hydrogen sulphide being removed by interactions with sulphoxylic acid (reaction I), with pyrosulphurous acid (reaction II), or with the sulphur dioxide of the sulphur dioxide–thiosulphate complex. The last reaction could be written $H_2S + [SO_2] = S(OH)_2 + S$, although it only occurs when the sulphur dioxide is combined or co-ordinated in a suitable manner (indicated by the square brackets).

We, like Foerster, suppose that the autoxidation involves the formation of thiosulphate and the breakdown of this by way of the polythionates. Our views differ more particularly as to the manner in which the thiosulphate originates and decomposes. We can find no evidence for the direct conversion of sulphoxylic acid into thiosulphuric acid, which is postulated by Foerster, and do not believe that it occurs (see pp. 1405, 1406, and 1439). The breakdown of thiosulphuric acid will be considered in the next section. Foerster considers that pentathionic acid is the first polythionic acid to be formed from thiosulphuric acid, whereas we consider that trithionic acid is first formed (reaction IX).

During the stage of autoxidation (reactions VII and VI), where thiosulphate is forming, the acidity or hydrogen-ion concentration increases, and addition of acid is consequently unfavourable to the reaction. On this account, bisulphite solutions undergo autoxidation much more rapidly than do sulphurous acid solutions.

This effect of the hydrogen ion is connected with its influence on the equilibria $H^{\cdot} + HSO_3' \rightleftharpoons H_2SO_3 \rightleftharpoons H_2O + SO_2$. The more acid the solution, the greater the proportion of sulphur dioxide present, and since the autoxidation becomes correspondingly slower, this favours the view that sulphur dioxide is not one of the primary

reactants. The well-known photochemical change $3SO_2 = 2SO_3 + S$ will not take place if the gas is absolutely dry (Coehn and Becker, *Z. physikal. Chem.*, 1910, **70**, 89), so that possibly even in this case the reaction follows a similar course to that outlined above, in the film of moisture adsorbed on the surface of the containing vessel.

Liquids other than water may be able to bring about the reaction, as in the somewhat similar case of the interaction of hydrogen sulphide and sulphur dioxide (Matthews, J., 1926, 2270). The view that pyrosulphurous acid is one of the primary reactants in the autoxidation of sulphurous acid is strengthened by the observations of Bennett (J., 1922, **121**, 1794), who found that sulphur, or even hydrogen sulphide, was liberated when sodium sulphite or pyrosulphite, in the solid state or in saturated solution, was added to hot concentrated sulphuric or phosphoric acid. Sulphur dioxide or its saturated solution in water would not act in this way. Under Bennett's conditions, the various stages in the autoxidation are passed through very rapidly, and it is not surprising that only the use of salts enables a sufficient concentration of pyrosulphurous acid to be obtained to make this possible.

It seems probable that, whenever sulphurous acid is reduced in presence of water, the reduction proceeds normally through the stage of hydrosulphite and not directly to sulphur or hydrogen sulphide. These would be products of decomposition of hydrosulphurous, sulphoxylic, or thiosulphuric acid. In certain cases the last may be the second step in the reduction, as in the electrolytic reduction already referred to (K. Jellinek and E. Jellinek, *loc. cit.*). Instances of reactions involving sulphurous acid which can be so accounted for are numerous (Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1913—14, **5**, 187; Durrant, J., 1915, **107**, 622; Wardlaw and Clews, J., 1920, **117**, 1093; Wardlaw, Carter, and Clews, *ibid.*, p. 1241; Wardlaw and Pinkard, J., 1922, **121**, 210; Stewart and Wardlaw, *ibid.*, p. 1481; Rogers, J., 1926, 254; Carter, *J. Soc. Chem. Ind.*, 1926, **45**, 207T; Wardlaw, *ibid.*, p. 210T).

Bichowsky (*J. Amer. Chem. Soc.*, 1922, **44**, 116) has shown that at high temperatures (527—613° Abs.) the hydrolysis of sulphur leads to equilibria involving hydrogen sulphide, sulphur dioxide, and sulphuric acid. These can be regarded as resulting from a combination of the hydrolytic equilibria occurring at the ordinary temperature with the autoxidation equilibria.

The Decomposition of Thiosulphuric Acid.

Numerous investigations on the action of acids upon thiosulphates have been published during the last few years, since we commenced

our own experiments, and we disagree with many of the conclusions. We find that thiosulphuric acid decomposes according to the three reversible reactions

$$H_2S_2O_3 \rightleftharpoons H_2SO_3 + S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VIII),$$
$$2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6 \quad . \quad . \quad . \quad . \quad . \quad (IX),$$
$$2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5 \quad . \quad . \quad . \quad . \quad . \quad (X).$$

Only reaction (VIII) is usually mentioned in text-books.

Reaction (IX).—The fact that hydrogen sulphide is invariably formed in small amounts when acid is added to thiosulphate solutions has escaped notice almost entirely. Spring and Levy (*Bull. Acad. roy. Belg.*, 1876, **42**, 103; Spring's collected researches, 1923, Vol. II, p. 1028) observed it, and so did Colson (*Bull. Soc. chim.*, 1880, **34**, 66). Colson attempted to discover the nature of the reaction and determined the ratio of hydrogen sulphide and sulphuric acid formed. He found that this was variable and seems to have concluded that the hydrogen sulphide was formed by the action of nascent sulphur on hot water. Of later workers, only Foerster, Lange, Drossbach, and Seidel (*loc. cit.*, pp. 245, 307) allude to it. They suppose that hydrogen sulphide is formed by a minor side-reaction, $H_2S_2O_3 + H_2O \rightleftharpoons H_2SO_4 + H_2S$, and do not bring this into their scheme of polythionate formation. The presence of hydrogen sulphide in standard sodium thiosulphate solutions has been attributed by Schulek (*Z. anal. Chem.*, 1926, **68**, 387) to bacterial action.

We find that hydrogen sulphide is always produced when acids or even water alone acts upon sodium thiosulphate. The gas is evolved if carbon dioxide is bubbled through, or if the thiosulphate is warmed with boric acid, whilst stronger acids liberate it readily. Little or no sulphuric acid is produced unless the mixture is boiled for a long time. It then results from the hydrolysis of tri- and tetra-thionic acids (Expt. H).

According to Jellinek (*Z. physikal. Chem.*, 1911, **76**, 257; see also Kolthoff, *Rec. trav. chim.*, 1924, **43**, 216) the oxy-acids of sulphur can be arranged in order of increasing strength in the series

$$H_2SO_3,\ H_2S_2O_4,\ H_2S_2O_3,\ H_2SO_4,\ H_2S_2O_6,\ H_2S_3O_6.$$

Di- and tri-thionic acids are of about the same strength, and so are thiosulphuric and sulphuric acids, whilst sulphurous acid is much the weakest of the series; hydrogen sulphide is still weaker. Reactions (VIII) and (IX) correspond to a definite decrease of hydrogen-ion concentration when proceeding from left to right. They should therefore tend to occur in acid solution, as we find to be the case, whilst they should be reversed in alkaline solution, which is true also.

That polythionic acids are formed by the action of acids on thiosulphates is fairly well known: Chancel and Diacon (*Compt. rend.*, 1863, **56**, 710; *J. pr. Chem.*, 1863, **90**, 55) seem to have been the first to observe it. We believe that our experiments show that reaction (IX) is the most important one by which these acids are formed. It is true that the amount of hydrogen sulphide liberated is very small in proportion to the amount of polythionic acids formed, but this is because reaction (VIII) is that which normally occurs to the greatest extent when acid acts upon thiosulphate. The hydrogen sulphide is thus liberated in presence of a large amount of sulphurous acid and destroyed by the same reactions which occur in the Wackenroder solution, which will be considered presently.

On this basis, trithionic acid becomes a primary, if not *the* primary, thionic acid produced.

The argument used by Foerster and Vogel (*loc. cit.*, p. 173) to show that penta- and not tri-thionic acid must be the primary thionic acid is unsound. According to our scheme, trithionic acid, formed by reaction (IX), combines with sulphur, formed by reactions (VIII), (II), and (I), to yield tetra- and penta-thionic acids. These are also formed by interaction with thiosulphate according to reactions (XIII) and (XIV). The fact that more thiosulphate than sulphite was consumed in Foerster and Vogel's experiments can thus be quite satisfactorily accounted for on the basis of our views.

Tetra- and penta- as well as tri-thionic acids are formed in the action of acids on thiosulphates, but the points which arise in this connexion will be discussed in the next section, which deals with the Wackenroder reaction.

Spring and Levy (*loc. cit.*) are the only authors who have attached any importance to the liberation of hydrogen sulphide, and who have assumed that polythionates result from trithionate formed in the manner just indicated. Of the greatest significance in this connexion is the fact that in alkaline solution the converse change occurs, alkali sulphide and trithionate reacting to form thiosulphate (Chancel and Diacon, *loc. cit.*).

We consider that there is overwhelming evidence that a reaction $H_2S_2O_3 + H_2O \rightleftharpoons H_2SO_4 + H_2S$ does not occur in either direction. The direct formation of sulphuric acid and hydrogen sulphide from thiosulphuric acid would correspond to a small increase in hydrogen ions, so that, if it is possible, it should be favoured by alkali and hindered by acid, whilst the formation of thiosulphate from sulphate and sulphide should be favoured by acidic conditions. Now we have found that in alkaline solutions mixtures of sulphate

and sulphide do not react to form thiosulphate, nor does thiosulphate yield sulphate and sulphide [see Expt. I, (i), (ii), and (vi)]. There seem to be only two ways of explaining these facts: either (*a*) the chemical inertia of the system is so great that unstable conditions persist more or less indefinitely, or (*b*) thiosulphate is not directly related to sulphate and sulphide in the manner indicated by the above equation.

There is considerable evidence in support of (*b*). The precipitation of sulphides of metals by the action of soluble thiosulphates on solutions of their salts, or by decomposition of previously-formed thiosulphates of the metals, is usually supposed to occur in such a way as to give sulphide and sulphate directly, *e.g.*, $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$, and a similar decomposition of thiosulphuric acid has been inferred. The same result could, however, be reached *via* the trithionate, *e.g.*,

$$2Ag_2S_2O_3 = Ag_2S + Ag_2S_3O_6; \; Ag_2S_3O_6 + 2H_2O = Ag_2S + 2H_2SO_4.$$

Since the trithionates of the heavy metals are nearly as unstable as the thiosulphates, it is difficult to settle this point with simple thiosulphates, although Fogh (*Compt. rend.*, 1890, **110**, 524) has shown quite clearly that when lead thiosulphate is boiled with water it yields, in the first instance, sulphide and trithionate. Fogh states that this decomposition into trithionate can occur quantitatively without any side reactions, but we have always found some decomposition of trithionate with consequent formation of sulphate and liberation of sulphur dioxide. It is certain, however, that the main reaction is that which yields trithionate. With double thiosulphates, it is easier to demonstrate that trithionate is formed, and Spring (*Bull. Acad. roy. Belg.*, 1874, **37**, 45; *op. cit.*, Vol. 2, p. 966) showed that solutions of the double thiosulphates of an alkali metal and silver, mercury, or lead yield on boiling silver, mercury, or lead sulphide and alkali trithionate. Conversely, lead sulphide on digestion with potassium trithionate was converted into lead thiosulphate. When boiled with less than the equivalent amount of alkali, lead thiosulphate is largely converted into trithionate [Expt. I, (vii)], and also when boiled with dilute acetic acid [Expt. I, (viii)]. We find that weakly alkaline solutions of sodium thiosulphate on boiling yield sulphide and trithionate, but only a trace of sulphate. If they are boiled with sodium plumbite, lead sulphide is precipitated and trithionate remains in solution, which is in agreement with Spring's results (Expt. I).

With strongly alkaline solutions of thiosulphate, the above reaction would not be expected to occur to any extent, for, in the equilibrium (IX), increased alkalinity favours the formation of

thiosulphate. A minute trace of sulphide always seems to be formed, however [Expt. I, (iii)].

Since trithionate on hydrolysis can yield sulphate, sulphite, and thiosulphate (pp. 1421, 1422), and thiosulphate yields trithionate, it follows that there are relationships, although indirect ones, between thiosulphate, sulphide, and sulphite on the one hand, and thiosulphate, sulphide, and sulphate on the other. The position can be seen from a consideration of the reactions

$$2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6 \overset{H_2O}{\rightleftharpoons} 2H_2S + H_2S_2O_7 \overset{H_2O}{\rightleftharpoons} 2H_2S + 2H_2SO_4 \quad \text{(i)}$$

$$\left.\begin{aligned} 2H_2S_2O_3 &\rightleftharpoons H_2S + H_2S_3O_6 \\ 2H_2S_3O_6 &\overset{H_2O}{\rightleftharpoons} H_2S_2O_3 + 4H_2SO_3 \end{aligned}\right\} 3H_2S_2O_3 \overset{3H_2O}{\rightleftharpoons} 2H_2S + 4H_2SO_3 \quad \text{(ii)}$$

From (i) it is seen that in alkaline solution the equilibria of its constituent reactions lie right over to the left as regards the change of thiosulphate into sulphide and trithionate, and completely to the right as regards the hydration of pyrosulphuric acid. For this reason, both ends of the reaction chain (i) appear equally stable in alkaline solution. Only in very strong sulphuric acid solution is any change in the direction of trithionate and thiosulphate possible.

Conditions are somewhat similar as regards (ii). In alkaline solution, the positions of equilibria are well to the left as regards the thiosulphate–trithionate reaction, and well to the right as regards the conversion of trithionate into sulphite and thiosulphate (which occurs in the steps discussed on p. 1447), so that here also it is found that thiosulphate shows no tendency to be hydrolysed to sulphide and sulphite, whilst, on the other hand, sulphide and sulphite will not react to yield thiosulphate [Expt. I, (iv) and (v)].

If only the summation equations $H_2S_2O_3 + H_2O \longrightarrow H_2S + H_2SO_4$ and $3H_2S_2O_3 + 3H_2O \longrightarrow 2H_2S + 4H_2SO_3$ are considered, quite erroneous ideas are formed.

Foerster and Mommsen (*Ber.*, 1924, **57**, 258; see also Foerster and Vogel, *loc. cit.*, p. 168) found that sodium hydrogen sulphide and bisulphite react smoothly to yield sodium thiosulphate: $2NaHS + 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O$. This summation equation has the same form as (ii) above, but it would seem that it represents a mechanism entirely different from that considered above. In all probability, Foerster and Mommsen's synthesis of thiosulphate involved reactions (II*b*), (I*b*), and (VIII*b*), occurring in succession. Here again, since alkali strongly favours thiosulphate in reaction (VIII) and the mixture of sulphide and sulphite in reaction (ii), we have the curious position that in alkaline solution both thiosulphate and also the mixture of sulphide and sulphite are

equally stable. Only in the neighbourhood of the neutral point is synthesis of thiosulphate possible by this method. We have found that sulphide and sulphite do not react in alkaline solution [Expt. I, (iv) and (v)].

Barium thiosulphate decomposes very slowly when boiled with water. Considerable quantities of polythionates are formed, but relatively little sulphate. The formation of barium sulphate equivalent to the barium thiosulphate would be expected if thiosulphuric acid decomposed according to the scheme $H_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + H_2S$, in which case, moreover, the decomposition should be greatly accelerated by the presence of barium, as it is by the presence of salts of copper, silver, and mercury, even after allowance has been made for the fact that barium sulphate is not nearly so insoluble as the sulphides of these metals.

An experiment due to Muck (*Ber.*, 1871, **4**, 446) seems at first sight to show that direct action of hydrogen sulphide on sulphuric acid *is* possible. This author found that, on boiling manganese sulphide with a solution of ammonium sulphate, ammonia and hydrogen sulphide were expelled and trithionate was formed, although only in small amount. He gives no indication of the amount of trithionate formed and does not prove that it was not thiosulphate. It is clear that in this experiment the manganese sulphide serves merely as a source of hydrogen sulphide, which is liberated by the action of the acid produced from the ammonium salt by hydrolysis. We have repeated the experiment and find that it is thiosulphate which is produced, not trithionate. The amount formed is exceedingly small if one takes precautions to exclude air as thoroughly as possible. It is not easy to prevent the formation of a small amount of black oxide of manganese—a sure sign of oxidation—and the thiosulphate is probably formed by atmospheric oxidation of hydrogen, or possibly ammonium, sulphide, this oxidation being perhaps catalysed by the manganese oxide. It is known that atmospheric oxidation of ammonium sulphide solutions does give rise to thiosulphate. We found that an old ammonium sulphide solution, which had deposited sulphur and lost its colour, had become a strong solution of ammonium thiosulphate (Expt. J).

Hydrogen sulphide and strong sulphuric acid interact, especially when hot, to produce sulphur and sulphurous acid, and this is generally represented by means of the equation $H_2S + H_2SO_4 \longrightarrow H_2SO_3 + H_2O + S$. At the ordinary temperature, the sulphuric acid has to be almost $25N$ before any separation of sulphur occurs on passage of hydrogen sulphide. One would have expected interaction at lower concentrations if non-ionised sulphuric acid were the active agent in the oxidation. It seems much more likely that

it is pyrosulphuric acid which reacts with the hydrogen sulphide in the first instance, and that the oxidation of the hydrogen sulphide by strong sulphuric acid takes place in several steps, the first of which consists in the formation of trithionic acid according to the equation

$$H_2S_2O_7 + H_2S \rightleftharpoons H_2S_3O_6 + H_2O \quad . \quad . \quad . \quad (XI)$$

It is probable that pyrosulphuric acid is present to some extent in acid as concentrated as 25*N*, but it is scarcely likely to be present at much lower concentrations.

Hydrolysis of the trithionic acid in the manner discussed on p. 1447 could yield sulphurous acid and thiosulphate, which would itself give sulphurous acid and sulphur. Sulphur could also be formed by interaction of hydrogen sulphide and the intermediate products of the hydrolysis. We consider that we have obtained small quantities of trithionic acid by the action of hydrogen sulphide on sulphuric acid of such a strength that sulphur is just not deposited when a current of hydrogen sulphide is passed through (Expt. K).

Trithionic acid must be regarded as being thiopyrosulphuric acid, and the hydrolysis of heavy-metal trithionates would yield pyrosulphuric acid in the first instance, and not two mols. of sulphuric acid as shown on p. 1418. On the above basis, the remarkable stability of thiosulphate towards alkali becomes intelligible,

Since an equilibrium $H_2S_2O_3 + H_2O \rightleftharpoons H_2S + H_2SO_4$ does not occur in any circumstances, there is no tendency for thiosulphate to be decomposed in such a manner by alkali, and likewise no possibility of interaction of sulphide and sulphate.

It is to be noted that in the equilibrium (IX) thiosulphuric and trithionic acids are of approximately the same strength, whilst hydrogen sulphide is much weaker. Alkali therefore shifts this equilibrium in favour of thiosulphate, and it is only in feebly alkaline solutions that there is any appreciable decomposition into sulphide and trithionate. Under more alkaline conditions, sulphide and trithionate readily yield thiosulphate, which is thus very stable in presence of strong alkali.

There is a difficulty in connexion with the hydrolysis of trithionates which has been pointed out by Foerster and Hornig (*Z. anorg. Chem.*, 1922, **125**, 119). Both in weakly alkaline and in weakly acid solutions, the hydrolysis of trithionic acid follows a course which can be represented by the equation $H_2S_3O_6 + H_2O \longrightarrow H_2SO_4 + H_2S_2O_3$. This hydrolysis is enormously accelerated by salts of copper, silver, and mercury with precipitation of the sulphides of these metals. This would be explicable, if the above hydrolysis is reversible, by the disturbance of the equilibrium caused by decom-

position of the thiosulphuric acid brought about by the insolubility of the metal sulphides precipitated. Against this view of the matter is the fact that the presence of added sulphate does not seem to slow down the rate of hydrolysis, whilst the presence of barium salts does not appreciably accelerate it, as might have been expected in view of the insolubility of barium sulphate.

The following is a possible way out of the difficulty: Trithionic acid is an equilibrium mixture of the two forms

$$(a)\ SH{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftharpoons OH{\cdot}SO_2{\cdot}S{\cdot}SO_2{\cdot}OH\ (b)$$

both of which could equally well be formed from thiosulphuric acid by elimination of hydrogen sulphide; form (*b*) seems to be favoured by alkaline conditions, which would indicate that it is the more acidic of the two—possibly because of its greater symmetry. Under ordinary conditions of acidity both forms will be present, (*a*) predominating. Equilibrium between the two forms is probably established very rapidly. Hydrolysis of form (*a*) yields, in the first instance, hydrogen sulphide and pyrosulphuric acid, and it is not surprising that the hydrolysis is greatly accelerated by copper, silver, and mercury salts owing to the insolubility of the sulphides of these metals. There is, however, no reason why a barium salt should accelerate hydrolysis in this direction, for in the equilibria

$$H_2S_3O_6 + H_2O \rightleftharpoons H_2S + H_2S_2O_7 \overset{+H_2O}{\rightleftharpoons} H_2S + 2H_2SO_4$$

the pyrosulphuric acid would be hydrated nearly as quickly in absence of barium as in its presence, since the equilibrium would be almost entirely in favour of sulphuric acid except in very acid concentrated solutions. For a similar reason, sulphate ions have little influence on the rate of hydrolysis.

The results of Kurtenacker and Kaufmann (*Z. anorg. Chem.*, 1925, **148**, 43) and of Foerster and Hornig (*loc. cit.*, p. 86) show that under neutral and acid conditions and in absence of heavy metals the hydrolysis of trithionic acid yields chiefly sulphate and thiosulphate. In presence of sodium acetate, quantitative agreement with the equation $H_2S_3O_6 + H_2O \longrightarrow H_2SO_4 + H_2S_2O_3$ is obtained (Foerster, *ibid.*, 1925, **144**, 337). It does not necessarily follow, however, that this is the primary reaction.

Kurtenacker and Kaufmann (*loc. cit.*, p. 369) have shown that in strongly alkaline solutions the hydrolysis of trithionate yields no sulphate, but only sulphite and thiosulphate: $2H_2S_3O_6 + 3H_2O \longrightarrow H_2S_2O_3 + 4H_2SO_3$. We consider the possible mechanism of this change on p. 1447. With decreasing alkalinity, sulphate is formed as well as sulphite and thiosulphate. In presence of sodium acetate, *i.e.*, under practically neutral conditions, sulphate and thiosulphate

are formed in equimolecular proportion, as Foerster showed. Rapid hydrolysis of trithionate in strongly acid solution yields more than one-third of the original sulphur in the form of sulphate. This agrees with the views expressed above, but does not prove that they are correct, for the extra sulphate might possibly be derived from polythionates formed by the Wackenroder reaction from hydrogen sulphide and sulphur dioxide, which are also formed during the hydrolysis. We do not think this is very likely, however (Expt. L).

We believe that trithionate never yields sulphate and thiosulphate directly on hydrolysis (which is why neither barium nor sulphate ions influence the reaction appreciably). Form (*a*) yields hydrogen sulphide and pyrosulphuric acid only, in the first instance, whilst form (*b*) is hydrolysed in the manner discussed on p. 1447. This in three steps leads to the reaction actually realised in strongly alkaline solution: $2H_2S_3O_6 + 3H_2O \longrightarrow H_2S_2O_3 + 4H_2SO_3$. Now sulphoxylic acid is an intermediate product in the hydrolysis of the (*b*) form, and would react with hydrogen sulphide formed on hydrolysis of form (*a*). If forms (*a*) and (*b*) were present in equal proportion and hydrolysed at the same rates, we should have the following combinations of reactions:

$$\begin{aligned}
\text{(Two steps)}\quad & H_2S_3O_6 + 2H_2O \rightleftharpoons 2H_2SO_4 + H_2S \\
\text{(Two steps)}\quad & H_2S_3O_6 + 2H_2O \rightleftharpoons 2H_2SO_3 + (HO)_2S \\
& H_2S + (HO)_2S \rightleftharpoons 2S + 2H_2O \\
& 2H_2SO_3 + 2S \rightleftharpoons 2H_2S_2O_3 \\
& 2[H_2S_3O_6 + H_2O \rightleftharpoons H_2SO_4 + H_2S_2O_3]
\end{aligned}$$

This balanced state of the two modes of hydrolysis seems to occur in neutral solution.

It is noteworthy in connexion with the above suggestions that hydrogen sulphide is always formed during the acid hydrolysis of trithionate, as was noticed by Kessler (*Pogg. Ann.*, 1848, **74**, 262). The fact that it is noticeable more particularly at the very commencement of the action suggests that it is, in the main, a real primary product rather than a product of decomposition of the thiosulphate.

Needless to say, and as Foerster and Hornig and Kurtenacker and Kaufmann have shown, the other polythionic acids are formed during the acid hydrolysis of trithionate as in all acid decompositions of sulphur acids, but these are due to later changes than those now being discussed. In Expt. M we record two hydrolytic experiments which extend Kurtenacker and Kaufmann's results.

Reaction (VIII).—Under most conditions, reaction (VIII) occurs

to the largest extent. It involves a perfectly definite equilibrium, such that in alkaline solution the thiosulphate is very stable. On this account, thiosulphate is readily formed by boiling alkaline sulphite solutions with sulphur. Nevertheless, even in the alkaline solutions there may be a perfectly definite although very small dissociation into sulphite and sulphur. If alkaline thiosulphate solutions containing alkali sulphide are boiled in absence of air, they become deep yellow owing to formation of polysulphide, the extra sulphur for which is obtained from the thiosulphate. A similar result is obtained by boiling an alkaline thiosulphate solution with sodium formaldehydesulphoxylate. The yellow solution obtained gives an immediate precipitate of lead sulphide with lead plumbite. This is rather an elegant method of showing that sulphide is formed on alkaline hydrolysis of sulphoxylate (compare p. 1403).

The equilibrium between sulphide and thiosulphate may be written $Na_2S + Na_2S_2O_3 \rightleftharpoons Na_2S_2 + Na_2SO_3$, although higher polysulphides might result as well. Such a reaction does not necessarily involve any dissociation of thiosulphates into sulphite and sulphur. There can be little doubt that it is because of such equilibria that a trace of hydrogen sulphide greatly accelerates the reaction between sodium sulphite and sulphur. We have found that sometimes there is a long delay before sulphur begins to dissolve in boiling sodium sulphite solution, and in such cases the effect of passing a few bubbles of hydrogen sulphide into the solution is very marked; once the reaction has commenced it proceeds smoothly. The catalytic action of sulphide has been referred to recently by Watson and Rajagopalan (*J. Indian Inst. Sci.*, 1925, **8**, A, 275), and had been previously noted by Hargreaves and Dunningham (*J. Soc. Chem. Ind.*, 1923, **42**, 147T). Alkali also catalyses the reaction owing to the production of sulphide by hydrolysis of the sulphur. It must be supposed that sodium sulphide or hydrogen sulphide is more efficient in detaching atoms of sulphur from solid sulphur than is sodium sulphite.

Holleman (*Rec. trav. chim.*, 1895, **14**, 71) considered that the decomposition of thiosulphuric acid into sulphur and sulphurous acid followed a unimolecular course, although he recognised that the figures with which he supported this view indicated some complication. He does not seem to have considered the possibility of a bimolecular reaction, although his figures give better values for such a reaction.

His method was to determine by an iodine titration the amount of decomposition which had occurred in sodium thiosulphate solutions of different concentrations one minute after mixing with the equivalent amount of hydrochloric acid. His three experiments

are given below, with the values of k calculated for uni- and bi-molecular reactions.

Mixture used.	$k_{uni.}$	$k_{bi.}$
M-$Na_2S_2O_3$ added to $2M$-HCl	0·437	1·124
$M/2$-$Na_2S_2O_3$ added to M-HCl	0·258	1·209
$M/5$-$Na_2S_2O_3$ added to $2M/5$-HCl	0·068	0·717

The correct values for k cannot be calculated from Holleman's data. He assumed, erroneously, that when decomposition was complete the final value of the iodine titre would be twice the initial titre, and on this basis he calculated the concentration of thiosulphate left after one minute. The true values are less than those used in the above calculations, for, owing to polythionate formation, thiosulphate disappears more quickly than is indicated by the increase in the iodine titre. We find that, instead of increasing to double the original titre, the final titre may be only 20—80% greater.

As it is now generally accepted that unimolecular reactions are very uncommon (see, *e.g.*, Hinshelwood and Topley, J., 1924, **125**, 393), we have examined the kinetics of the decomposition of thiosulphuric acid more fully. The method used was to titrate acidified solutions after different intervals of time with standard iodine solution, continuing until the iodine titre reached a maximum value and became approximately constant or even decreased.

It is evident from the figures quoted (Expt. N) that the maximum value of the iodine titre is smallest for the most dilute solutions, and tends to increase both with increasing concentration of thiosulphate and with increasing acidity. Even in the most acid solution examined, the maximum titre was only 75% greater than the initial. If thiosulphuric acid decomposed only according to reaction (VIII), the iodine titre would eventually become doubled; if the decomposition was entirely according to reaction (IX), the titre would remain unaltered. If both modes of decomposition occur together, then reactions (II*b*) and (I*b*) follow as a matter of course, and, provided reactions (VIII) and (IX) occur in the right proportion, the iodine titre might fall to zero.

The greater part of the sulphurous acid formed in reaction (VIII) becomes either pyrosulphurous acid or sulphur dioxide and, when extended to include these changes, reaction (VIII) corresponds to a greater decrease of acidity than does reaction (IX). It follows that the more acid the conditions under which thiosulphuric acid decomposes, the more may reaction (VIII) be expected to predominate as compared with reaction (IX) (compare pp. 1430—31). The increase in the maximum iodine titration with increasing acidity, in the experiments under consideration, seems to be mainly due to such an increase in the relative importance of reaction (VIII).

The reason for the existence of a maximum iodine titre at all must be considered. From the experiments quoted, it will be seen that it is practically only in the cases where acid and thiosulphate are mixed in equivalent amounts that well-marked maxima exist. Moreover, in these cases the maxima occur at a very early stage of the reaction. In experiments where excess of acid was used, the iodine titre slowly approached a limiting value, and if it subsequently diminished at all it did so very slowly. In those cases where thiosulphate and acid were mixed in equivalent amounts, the acidity of the mixed solution at the commencement may be considered as being due entirely to thiosulphuric acid, which is a strong acid. As decomposition proceeds, according to reactions (VIII) and (IX), supplemented by reactions (II*b*) and (I*b*), a considerable decrease of acidity occurs. Because of this diminution in the acidity of the solution, reaction (IX) tends to increase relatively to reaction (VIII) as the decomposition proceeds, and this could account for the experimentally observed maximum iodine titre, for not only does reaction (IX) itself cause no increase in the original titre, but, in consequence of reactions (II*b*) and (I*b*), it will lead to the destruction of some of the accumulated sulphurous acid and so cause a decrease in the iodine titre.

Even in very weakly acid solutions, reactions (II*b*) and (I*b*) in conjunction seem to occur with great rapidity owing to the considerable decrease in acidity which they produce, and in all but the weakest and least acid solutions we may safely assume that none of the iodine reduction is due to either hydrogen sulphide or sulphoxylic acid. It is because of the rapidity of these reactions that hydrogen sulphide cannot be detected by means of lead salts (Holleman, *loc. cit.*) or even silver salts in acidified thiosulphate solutions, but it can, in favourable circumstances (Expt. H), be detected in the vapours given off from such solutions on boiling, owing to the fact that hydrogen sulphide and sulphur dioxide can coexist in presence of water vapour and need liquid water for interaction to occur (Matthews, *loc. cit.*).

It will be found that the combination of reactions (VIII) and (IX) with (II*b*) and (I*b*) * just sufficient to remove all the hydrogen sulphide formed by reaction (IX) yields the summation equation

$$10H_2S_2O_3 \longrightarrow 4H_2S_3O_6 + 4S_2 + 6H_2O,$$

8 mols. of thiosulphuric acid having decomposed according to reaction (IX), and 2 mols. according to reaction (VIII). Now it is clear that, for any increase at all to occur in the iodine titre of the

* Bearing in mind that $H_2S_2O_5$ is formed from $2H_2SO_3$ by loss of water, whilst HO·S·O·S·OH yields $2S(OH)_2$ by addition of water.

decomposing thiosulphate solution, an additional 10 mols., at least, of thiosulphuric acid must decompose according to reaction (VIII) in the early stages of the decomposition. The 20 mols. of thiosulphuric acid would require 20 atoms of iodine for oxidation to tetrathionate. If, however, 10 decomposed as in the above equation, the products would not react with iodine, but the 10 mols. of sulphurous acid formed by the remaining 10 mols. of thiosulphuric acid would require 20 atoms of iodine for oxidation to sulphate. It would appear that in all the cases we have studied, more than 50% of the decomposition took place in accordance with reaction (VIII), and usually a much larger proportion.

It is evident that if the sulphoxylic acid formed by reaction (II*b*) did persist at all, it would have a large effect on the iodine titre, since 1 mol. of sulphoxylic acid requires 4 atoms of iodine to oxidise it to sulphuric acid. It would be possible for a maximum in the iodine titre to arise, quite apart from any change in the relative proportions in which reactions (VIII) and (IX) took place, from an accumulation of sulphoxylic acid in the early stages of the decomposition of thiosulphuric acid, followed by its destruction by interaction with hydrogen sulphide at a later stage. This is unlikely to occur except in dilute and weakly acid solutions, but we have satisfied ourselves that even in solution (*c*) (see Table V) no sulphoxylic acid can be detected. This solution was found to behave exactly like thiosulphate towards methylene-blue (see p. 1435), whilst with ammoniacal silver nitrate it gave no metallic silver, as would sulphoxylic acid, but after many hours' standing it gave an amount of silver sulphide which more or less corresponded to the thiosulphate left undecomposed at the moment of adding the ammoniacal silver nitrate.

During the early stages of the decomposition of thiosulphuric acid, a certain proportion of tetra- and penta-thionic acids will have been formed in many cases owing to reactions (XIV*a*) and (XV*a*)—and perhaps (XII*a*) and (XIII*a*). Towards the end of the decomposition, the higher polythionates will have become less stable owing to the general decrease of acidity (see p. 1448), and reactions (XIV*b*) and (XV*b*) will tend to take place. Decomposition of the thiosulphuric acid so produced would occur in accordance with reaction (IX), whilst the hydrogen sulphide formed would cause further destruction of sulphurous acid. It is probable that some of the very slow decrease in the iodine titre at the end of the decomposition is to be accounted for in this way.

Moreover, from the fact that more sulphate was formed in the latest stages of the (*b*) experiment (see Table V) than corresponds to the iodine titration, it would seem that slow hydrolysis of trithionate

under the influence of sulphurous acid sets in after an hour or less.

It is evident from the preceding discussion that, in those cases where a well-marked maximum occurs, decomposition of the thiosulphate will probably not be complete when this maximum is reached. The amount of thiosulphate still undecomposed is readily obtained by determining the sulphate present after the iodine titration, assuming that sulphurous and thiosulphuric acids had been the only substances present which reacted with iodine. This determination was made in a number of cases, the titrated solution being heated just to boiling immediately before adding the barium chloride. No appreciable hydrolysis of polythionates occurs under these conditions. The amounts of thiosulphate decomposed at earlier stages [x in the fourth columns of Table V, (a), (b), and (c)] were calculated from the values so found for the maxima, on the assumption that they were proportional to the iodine titre. Using these figures, the bimolecular velocity coefficients were calculated and surprisingly good values were obtained.

In the case of experiments (a) and (b), the sulphate estimation was made in each case after the iodine titration. The tables show that the rate of decomposition of thiosulphate, under the conditions of these experiments, increases very rapidly with increase in concentration of thiosulphate. In the very early stages of the decomposition the amount transformed in a given time is roughly proportional to the *square* of the thiosulphate concentrations, whilst the time taken to complete a certain fraction of the decomposition is, to a rough approximation, inversely proportional to the initial concentration of thiosulphate.

In those experiments where excess of hydrochloric acid was used, the influence of thiosulphate concentration was of the character just stated for a considerable proportion of the reaction, but where acid and thiosulphate were used in equivalent amounts, the figures show that during most of the decomposition the weaker solutions were decomposing at a greater rate than would be expected from the concentration, and this becomes more obvious as the decomposition proceeds.

It is probable that as reaction (IX) increases relatively to reaction (VIII) in the dilute, weakly acid solutions, the increased extent to which reactions (IIb) and (Ib) occur will have an appreciable accelerating effect on both reactions (VIII) and (IX), so that, as a whole, the decomposition of thiosulphate proceeds at a relatively enhanced rate.

When all the results summarised in Expt. N and discussed above are considered critically, they indicate that the decomposition of

thiosulphuric acid follows a bimolecular course over a considerable range. Some caution must, of course, be used in interpreting the results of reaction-velocity determinations with such complex systems as that under discussion.

It is admitted that the decomposition of thiosulphuric acid is a mixed reaction and due to two simultaneous primary changes (VIII) and (IX), but as, under the conditions studied, the change into sulphurous acid and sulphur represented 50—75% of the whole decomposition, such good agreement with the bimolecular formula could scarcely be obtained unless this change were bimolecular. In fact, the results support the view that both primary reactions are bimolecular. Reaction (VIII) must therefore be represented by the equation $2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2$. This seems to show that the sulphur unit concerned (we hesitate to call it a molecule) is S_2, and may explain why hydrogen sulphide catalyses the reaction between sodium sulphite and solid sulphur. Since hydrogen sulphide can combine with S_2 to form hydrogen trisulphide, whilst sodium sulphite can only combine with one atom of sulphur, 1 mol. of hydrogen sulphide could detach the S_2 unit from solid sulphur, whereas 2 mols. of sodium sulphite would have to co-operate. Since hydrogen disulphide also exists, the trisulphide could pass on its extra sulphur to sodium sulphite in two steps :

$$\begin{cases} H_2S_3 + Na_2SO_3 \rightleftharpoons Na_2S_2O_3 + H_2S_2 \\ H_2S_2 + Na_2SO_3 \rightleftharpoons Na_2S_2O_3 + H_2S. \end{cases}$$

It may be pointed out that our reaction (I) for the hydrolysis of sulphur suggests that sulphur acts as though composed of S_2 units.

The $\left[\begin{matrix} O & O \\ O & S \end{matrix} S\right]''$ ion of the thiosulphates is very stable, having a very small tendency to drop the second sulphur atom and become $\left[\begin{matrix} O \\ O \end{matrix} S O\right]''$. In dilute solutions of thiosulphuric acid which do not contain another acid, this should still be true. It is probably not until the hydrogen ions become attached to the S_2O_3'' ion by covalencies instead of electrovalencies that rapid decomposition of thiosulphuric acid begins. This occurs the more readily the greater the thiosulphate and hydrogen-ion concentrations. Dilute acid solutions should therefore contain unaltered thiosulphuric acid and its ions for some time. Now one of the most marked characteristics of the S_2O_3'' ion is that it can be readily oxidised to the S_4O_6'' ion. The great majority of oxidising agents which are not too violent actually oxidise thiosulphate to tetrathionate, but it is not commonly realised what a powerful reducing agent thiosulphate is. Spring [*Bull. Acad. roy. Belg.*, 1881, (iii), **1**, 106; *op. cit.*, Vol. II, p. 1109]

found that freshly acidified solutions of thiosulphate bleached indigo, and he attributed this to the presence of hydrosulphurous acid. There can be little doubt, however, that the bleaching is due to thiosulphuric acid, for we find that under suitable conditions either weakly or strongly acidified solutions of thiosulphate can be titrated quantitatively to tetrathionate, either with indigo or, much more conveniently, with methylene-blue. The reaction is bimolecular and is greatly accelerated by hydrogen ions. Litmus and methyl-orange are also reduced by the acidified thiosulphate solutions.

Gil and Beato (*Anal. Fis. Quim.*, 1924, **22**, 84) found that if sodium thiosulphate was added to concentrated hydrochloric acid, pure sodium chloride was precipitated, whilst the separated solution remained perfectly clear, without any deposition of sulphur, for many hours. They concluded that thiosulphuric acid became more stable the greater the acidity of the solution. This view in its simple form is contrary both to experience and to the principle of Le Chatelier. Were it true, then thiosulphate would become less stable in alkaline solution, which is not the case, whilst there can be no question that at low acidities thiosulphate decomposes the more quickly the greater the acidity.

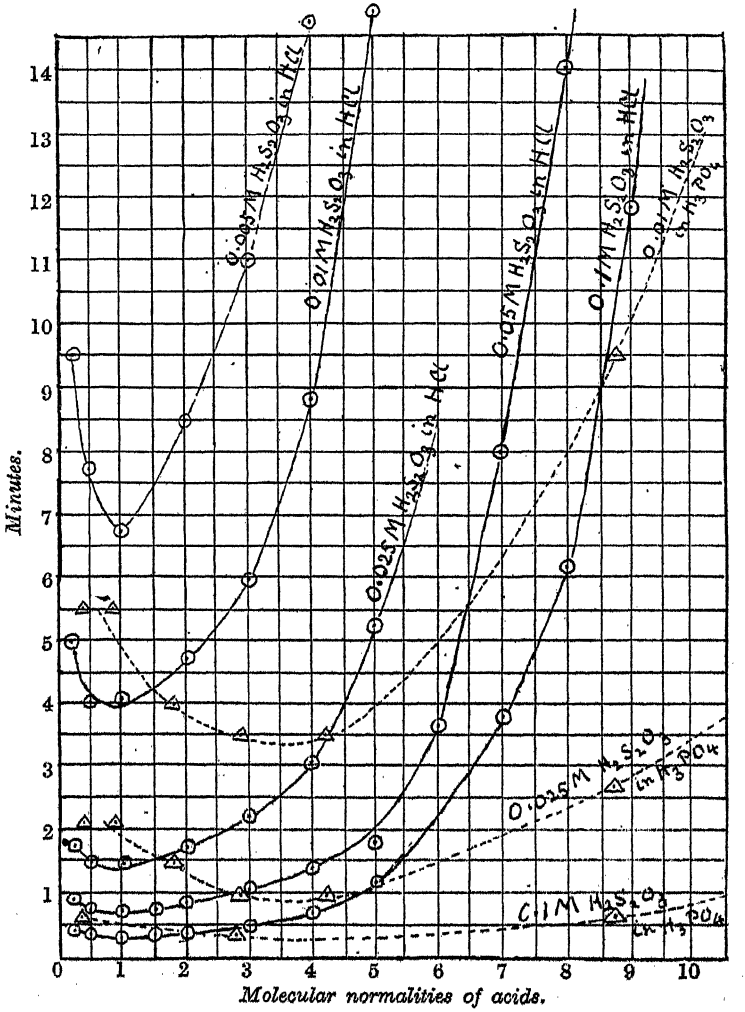
The non-appearance of sulphur does not show that no decomposition of thiosulphuric acid has occurred. Holleman (*loc. cit.*) showed that decomposition began as soon as thiosulphuric acid was liberated from its salts, even although no sulphur had separated. He considered that this was due to the sulphur liberated by reaction (VIII) remaining in colloidal solution, because an acidified thiosulphate solution, if neutralised before the time when separation of sulphur occurred normally, still deposited sulphur. On repeating his experiments, we confirmed these results, but we did not observe this separation of sulphur on neutralisation in all circumstances if the thiosulphate solutions were much weaker than those used by Holleman (see p. 1433).

When the time taken for the sulphur to become visible (compare Gaillard, *Compt. rend.*, 1905, **140**, 652; Oettingen, *Z. physikal. Chem.*, 1900, **33**, 1) is noted for solutions of increasing acidity, it is found to pass through a minimum, and with very high acidities no sulphur separates until after many hours, as in Gil and Beato's experiment. The minimum occurs in solutions which are approximately *N* in hydrogen-ion concentration, no matter what the thiosulphate concentration, as is well shown in Fig. 1; phosphoric acid has a similar effect to hydrochloric acid when allowance is made for its much lower hydrogen-ion concentration (Expt. O).

The delay in the separation of sulphur at high acidities is easily

explained on the basis of our theory of the decomposition of thiosulphuric acid. It is not due to strong hydrochloric acid retarding the change $HS_2O_3' \longrightarrow HSO_3' + S$, as supposed by Foerster and Vogel

FIG. 1.



Times of appearance of sulphur in acidified thiosulphate solutions. All normalities to be multiplied by ½ to obtain actual concentrations.

(*loc. cit.*, p. 183). Both reactions (VIII) and (IX) are accelerated by acid, the former more so than the latter, owing to the fact that the greater part of the sulphurous acid becomes sulphur dioxide. Reaction (VIII), when extended to include the formation of sulphur

dioxide, corresponds to a greater decrease of acidity than does reaction (IX), hence the preferential influence of hydrogen ions on (VIII). The experiments we have already quoted (Expt. N) bear out the correctness of this deduction.

The simultaneous occurrence of reactions (VIII) and (IX) brings in reactions (II*b*) and (I*b*) which are also favoured by acid. Tetra- and penta-thionic acids are formed from trithionic acid either by direct addition of sulphur,

$$H_2S_3O_6 + S \rightleftharpoons H_2S_4O_6 \; (2H_2S_3O_6 + S_2 \rightleftharpoons 2H_2S_4O_6) \; . \quad . \quad (XII)$$
$$H_2S_4O_6 + S \rightleftharpoons H_2S_5O_6 \; (2H_2S_4O_6 + S_2 \rightleftharpoons 2H_2S_5O_6) \; . \quad . \quad (XIII)$$

or by interaction with thiosulphuric acid,

$$H_2S_3O_6 + H_2S_2O_3 \rightleftharpoons H_2S_4O_6 + H_2SO_3 \; . \quad . \quad . \quad (XIV)$$
$$H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3 \; . \quad . \quad . \quad (XV)$$

and all these reactions are favoured by acidity (see p. 1448). The occurrence of these last four reactions represents, in the aggregate, a large decrease of hydrogen-ion concentration and so is greatly favoured by acidity. The more they occur the less the extent to which reaction (VIII*a*) can occur, but this effect on the decomposition of thiosulphuric acid as a whole does not become apparent until a reasonable amount of trithionic acid has been formed by reaction (IX).

That the effect is real is readily shown by acidifying under similar conditions pure thiosulphate or a mixture of thiosulphate with tri- or tetra-thionate. The mixtures take much longer than the pure thiosulphate to give a deposit of sulphur (Expt. P).

We are inclined to think that reactions (XIV) and (XV) are much more important than reactions (XII) and (XIII) for building up the polythionates. We could obtain no certain proof that colloidal sulphur, prepared by Svedberg's method (*Z. Chem. Ind. Koll.*, 1909, **4**, 49), was absorbed at all by trithionic acid, but sulphur liberated in presence of trithionic acid, by the interaction of hydrogen sulphide and iodine, was readily taken up to form tetrathionate. No satisfactory conversion of tetrathionate into pentathionate could be obtained by this method (Expt. Q). A solution of sulphur in benzene seemed to have no action on either trithionate or tetrathionate.

Increase in hydrogen-ion concentration thus tends, on the one hand, to diminish the time required for the separation of sulphur in so far as it accelerates reaction (VIII*a*), but, on the other hand, it lengthens the time required by favouring all the opposing reactions mentioned above. In such circumstances, the occurrence of a minimum time of appearance of sulphur at a fairly definite acidity is only to be expected.

All the reactions occurring in the acidified thiosulphate proceed with a diminution of acidity. They gradually become slower as the limiting concentrations of the several polythionic acids characteristic of the prevailing hydrogen-ion concentration are approached (see p. 1448). Since the hydrogen-ion concentration gradually diminishes, the system is never fully stable—readjustments are continually necessary which ultimately lead to the decomposition of the polythionic acids with separation of sulphur.

It is here appropriate to consider the marked influence of arsenious oxide in preventing separation of sulphur and promoting the formation of pentathionic acid from thiosulphate. This phenomenon was discovered by Salzer (*Ber.*, 1886, **19**, 1696) and has been applied by Raschig (*Z. angew. Chem.*, 1920, **33**, 260). It is known that sulphur oxidises arsenite to oxythioarsenate, and no doubt Salzer was right in thinking that the latter played an important part in the reaction. The oxythioarsenate would act in two ways. (1) Owing to its ready formation, it would prevent separation of sulphur from thiosulphuric acid by reaction (VIII). This would probably be due to the direct reaction $H_2S_2O_3 + H_3AsO_3 \rightleftharpoons H_2SO_3 + H_3AsO_3S$ (assuming that H_3AsO_3S is the only oxythioarsenate involved). The oxythioarsenate would yield its sulphur to trithionic acid, formed in the normal way by reaction (IX), to give tetra- and penta-thionic acids in two stages: $H_2S_3O_6 + H_3AsO_3S \rightleftharpoons H_2S_4O_6 + H_3AsO_3$, $H_2S_4O_6 + H_3AsO_3S \rightleftharpoons H_2S_5O_6 + H_3AsO_3$. (2) It could also take up any sulphur found by reactions (II) and (I) and pass it on as above: $H_3AsO_3 + S \rightleftharpoons H_3AsO_3S$ (or $2H_3AsO_3 + S_2 \rightleftharpoons 2H_3AsO_3S$).

Under favourable conditions, complete conversion of thiosulphate into pentathionate is theoretically possible with the help of small quantities of arsenious oxide, and very good yields are actually obtainable. It will be observed that the arsenious acid is really a vehicle for the handing on of sulphur to trithionic acid just as is sulphurous acid, the oxythioarsenic acid playing the same rôle in the one case as thiosulphuric acid in the other. There is also a superficial resemblance between the action of arsenious acid and of strong hydrochloric acid in preventing separation of sulphur. The reasons for the two actions are different, however, although both depend on the introduction or acceleration of reactions which use up sulphur more quickly than it is produced by reaction (VIII).

If dilute thiosulphate solutions are treated with less acid than corresponds to the minima in the curves of Fig. 1 and then quickly neutralised before sulphur becomes visible, separation of sulphur may be entirely prevented if the addition of alkali has been made an appreciable time before precipitation would normally occur. If, however, the alkali is added very shortly before separation of sulphur

would occur normally, its addition causes immediate separation of sulphur, and in such cases either alkali or lanthanum nitrate will produce a precipitate. Solutions to the right of the minima still give the reactions for colloidal sulphur with separation of sulphur on addition of alkali or lanthanum nitrate, but we believe that they also contain pentathionate (although this is difficult to prove), the proportion of pentathionate increasing with acidity and time and that of colloidal sulphur diminishing (Expt. R).

It is not possible to apply the neutralisation test to the very acidic mixtures, for if the whole amount of concentrated alkali needed for neutralisation is added suddenly, the heat liberated causes complications, whilst if neutralisation is effected slowly, one passes into the less acid regions, where sulphur separates rapidly. Neutralisation of such solutions is therefore incapable of throwing light on the conditions prevailing therein at the stage prior to separation of sulphur.

Reaction (X).—In the very acid solutions, not only is reaction (VIII) delayed, but so also is the formation of pentathionate, and in fact thiosulphuric acid seems to have become more stable, as Gil and Beato suggested. The peculiar facts can be satisfactorily accounted for in terms of a reaction

$$2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5 \quad . \quad . \quad . \quad . \quad . \quad (X)$$

It is obvious that such a reaction is theoretically possible, and it is to be noted that it would be extremely effective as a means of removing hydrogen ions. It is reasonable, therefore, to suppose that it may occur in very acid solution, but it may well occur to some extent under much less acid conditions, although in such circumstances the active mass of water will usually be so great that it could not proceed very far. It may be noted in this connexion that we have found that a strong zinc chloride solution will greatly delay the separation of sulphur from acidified thiosulphate. In one experiment, sulphur appeared after 6 minutes when zinc chloride was used, but after 35 seconds when the zinc chloride solution was replaced by an equal volume of water. The effect of zinc chloride is thus quite marked, but, as it only depends on a dehydrating action, it is naturally much less than the effect produced by strong hydrochloric acid, which depends on a hydrogen-ion action as well.

There is no reason why $H_2S_4O_5$ should not be much more stable towards loss of sulphur or of hydrogen sulphide than is the simple thiosulphuric acid—in fact we think it likely that it would be. As regards the direct loss of sulphur, it might be argued that, if we are right in supposing that in the case of thiosulphuric acid this occurs in such a way as to eliminate an S_2 unit: $2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2$,

then it should occur still more readily from $H_2S_4O_5$, where the thiosulphate molecules have already been brought together. But when the known weakness of the second-stage ionisation of sulphurous acid is considered in conjunction with the known tendency for sulphur to become co-ordinated with four atoms or groups, there are good reasons for thinking that the direct loss of sulphur by thiosulphuric acid is largely due to the fact that a hydrogen atom is able to take the place of the escaping sulphur atom.

If this is correct, the decomposition of thiosulphuric acid according to reaction (VIII) is to be regarded as giving rise to sulphur and sulphonic acid, not sulphurous acid:

$$2H_2\left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\S\end{matrix}\right] \rightleftharpoons 2H\left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\H\end{matrix}\right] + S_2.$$

This would be another reason for the great stability of the alkali-metal thiosulphates in neutral or alkaline solution, for the alkali-metal atoms cannot become co-ordinated in the same way as a hydrogen atom—their valencies are always electrovalencies.

In view of the fact that $H_2S_2O_5$, pyrosulphurous acid, is a strong acid, there would not be the same possibility of hydrogen taking the place of sulphur in the manner just indicated were $H_2S_4O_5$ to shed an S_2 unit. $H_2S_4O_5$ may therefore be expected to be very stable towards direct loss of sulphur, but in other directions it would react very much like thiosulphuric acid. This appears to be the case in its behaviour towards oxidising agents. Thiosulphate solutions which have been treated with a large excess of concentrated hydrochloric acid (Gil and Beato's solution) still reduce iodine. Titration with iodine at known intervals of time, in conjunction with subsequent determination of the sulphate present in the oxidised solution, has shown that thiosulphate (actually $H_2S_4O_5$, according to us) persists for a surprising length of time—much longer than in the case of less strongly acidified solutions (compare Expt. N). Even after 2 hours nearly 30% remained undecomposed (Expt. S).

The strongly acid thiosulphate solutions also exert a strong bleaching action on indigo, methylene-blue, litmus, and methyl-orange, and we find that they can be titrated smoothly and rapidly with methylene-blue (indigo can be used, but is not so satisfactory, as it reacts more slowly).

The amount of methylene-blue which is bleached is in close agreement with that required by the reaction

$$\underset{\text{(methylene-blue)}}{C_{16}H_{18}N_3SCl} + H_2S_4O_5 + H_2O = \underset{\text{(\textit{leuco}-methylene-blue)}}{C_{16}H_{19}N_3S} + H_2S_4O_6 + HCl,$$

or more probably (see Expt. T)

$$C_{16}H_{18}N_3SCl + S_4O_5'' + H_2O = C_{16}H_{19}N_3S,HCl + S_4O_6''.$$

The rate at which the methylene-blue is bleached is very greatly increased by rise of temperature. The strongly acidic bleached solutions are comparatively stable towards atmospheric oxidation, but the blue colour is at once restored by a drop or two of strong nitric acid, by hydrogen peroxide, or even by silver nitrate or silver acetate. This behaviour towards silver has prevented us from carrying out any direct estimation of the tetrathionate formed in the reaction between thiosulphate and methylene-blue. We have, however, isolated the *leuco*-methylene-blue formed in the reaction (Expt. T).

The only alternative explanation of the quantitative relationships between methylene-blue and thiosulphate found experimentally would seem to be that a colourless addition compound is formed between one molecule of methylene-blue and one of $H_2S_4O_5$ (or two molecules of $H_2S_2O_3$). Such an explanation appears to be completely ruled out by the fact that the bleached solutions remain colourless under the following treatments: (1) Dilution with air-free water; (2) boiling in absence of air; (3) cautious treatment with hydrogen sulphide or sulphur dioxide, which react with and destroy thiosulphate; (4) addition of formaldehyde, which forms trithioformaldehyde with thiosulphuric acid; or (5) long boiling with 5*N*-hydrochloric acid in absence of air—a complex containing thiosulphuric acid could scarcely remain undecomposed by such treatment. Lastly, it may be mentioned that the action of methylene-blue in preventing the separation of sulphur, which is dealt with in the next paragraph, would be difficult to account for on any other basis than tetrathionate formation.

Even in comparatively weakly acid solutions (of *N*-hydrogen-ion concentration, or even less) thiosulphate can be titrated with methylene-blue, apparently with the same end results as in very acid solutions. If the methylene-blue is added as fast as it is decolorised, no separation of sulphur occurs. This is owing to conversion of tetrathionate into pentathionate according to reaction (XV*a*) (compare Expt. P); but as thiosulphate is oxidised to tetrathionate, more is formed from pentathionate by reaction (XV*b*). As a consequence of this, almost complete conversion of thiosulphate into tetrathionate by methylene-blue is possible if sufficient time is taken and sulphur dioxide is not allowed to escape. Whether, in such weakly acid solutions, the reaction involves $H_2S_4O_5$ must remain undecided. It may occur in two steps, first the formation of an addition compound $H_2S_2O_3$–methylene-blue, and then the interaction of this with a second molecule of thiosulphuric acid.

It is very probable that the reaction between thiosulphate and

iodine is of this character and actually bimolecular. It is generally represented as being termolecular :

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2HI \text{ (or } 2S_2O_3'' + I_2 \longrightarrow S_4O_6'' + 2I').$$

In view of the rapidity with which it occurs, it cannot really be termolecular, but it could well occur in two stages, the first involving formation of $Na_2S_2O_3,I_2$ or S_2O_3,I_2'', and the second the reaction of this compound with a second thiosulphate molecule or ion. The iodine and methylene-blue would probably become attached to the outer sulphur atom of the S_2O_3 group, just as sulphur dioxide does in the yellow compounds, $Rb_2S_2O_3,SO_2$, etc.

Some determinations of the time required to bleach a constant amount of methylene-blue with varying concentrations of sodium thiosulphate, taken in excess, and of hydrochloric acid are in agreement with what we consider to be the mechanism of the reduction (Expt. U).

It is likely that the $H_2S_4O_5$ (or S_4O_5'') which acts on the methylene-blue results from the two reactions $2H^{\cdot} + 2S_2O_3'' \rightleftharpoons 2HS_2O_3'$ and $2HS_2O_3' \rightleftharpoons S_4O_5'' + H_2O$, which are equivalent to $2H^{\cdot} + 2S_2O_3'' \rightleftharpoons S_4O_5'' + H_2O$. The rate of bleaching of methylene-blue, dx/dt, would then be given by the expression $dx/dt = k'$ [methylene-blue] $[S_4O_5'']$ $= k$ [methylene-blue] $[S_2O_3'']^2[H^{\cdot}]^2$.

In other words, the rate of bleaching should be proportional to the square of the S_2O_3'' ion concentration, which, in dilute solutions, would be approximately equal to the thiosulphate concentration. If, then, in the solution under investigation, very little of the total thiosulphate was in the form of S_4O_5'', we should expect to find the rate of bleaching proportional to the square of the total thiosulphate concentration and also to the square of the hydrogen-ion concentration; but if practically all the thiosulphate were present as $H_2S_4O_5$ (or S_4O_5''), this would no longer be true, and the rate of bleaching would be directly proportional to the first power of the thiosulphate concentration (since the $H_2S_4O_5$ concentration would be simply half of this), and practically independent of the hydrogen-ion concentration. Intermediate results between these two extremes would correspond to the case where some thiosulphate was present as such and some as $H_2S_4O_5$.

From the results of Expt. U (Table VII), it is seen that, in the solutions of lowest acidity and lowest thiosulphate concentration, the times taken to bleach the constant amount of methylene-blue become closely proportional to the square of the (total) thiosulphate concentration. With the higher concentrations both of acid and of thiosulphate, the times of bleaching are intermediate between those required by a first-power and by a second-power effect of the

thiosulphate. In all solutions less than 2·3*N* with respect to hydrogen chloride, the rate of bleaching is approximately proportional to the total acid concentration, and therefore, in all probability, to the hydrogen-ion concentration. 4·75*N*-Acid has no more effect than 2·3*N*, *i.e.*, above 2·3*N* the reaction seems to become independent of hydrogen-ion concentration. 9·5*N*-Acid is found actually to delay the bleaching as compared with acid of half its strength. This effect has probably nothing to do with hydrogen ions, but may well depend upon such factors as increased viscosity. Rough measurements of the viscosities of 10*N*- and 5*N*-hydrochloric acid show that these are in the ratio of 1·46, whereas the corresponding ratio for 5*N*- and *N*-acid is 1·15, showing that a marked increase of viscosity occurs above 5*N*. That the acid acts according to approximately the first power of its concentration might be regarded as indicating an ordinary catalytic effect, but we prefer to consider that this is due to the fact that, in so far as thiosulphate is present as such, the bleaching reaction depends on the square of the acidity, but in so far as it is present as S_4O_5'', the bleaching is independent of the acidity, where we have no means of measuring S_4O_5'' and S_2O_3'' separately and have to express ourselves in terms of total thiosulphate.

It must be pointed out that even in the least acidic mixtures the concentration of acid was about 50 times that of the thiosulphate. We consider that the close agreement between these experimental results and the deductions made above furnishes evidence in favour of the real existence of the compound $H_2S_4O_5$, and it would seem that under the conditions of the experiments at least half the total thiosulphate was present as $H_2S_4O_5$.

In view of the fact that hydrogen sulphide reduces methylene-blue, one could explain the kinetic results obtained in the weaker and less acid solutions on the basis of such reduction, the hydrogen sulphide being derived from reaction (IX); for it will be found that the rate of reduction in this case would be given by the expression

$$dx/dt = k'[\text{methylene-blue}][H_2S] = k[\text{methylene-blue}][S_2O_3'']^2[H^\cdot]^2$$

which is of the same form as that obtained above.

To explain the kinetic results obtained in the stronger and more acid solutions on this basis, it would be necessary to assume that a large proportion of hydrogen sulphide was present, which is certainly not correct. Moreover, both theory and experiment (see p. 1425 and Expt. N) indicate that reaction (IX) tends to predominate at low acidities, not high ones. It may be concluded,

therefore, that the reduction of methylene-blue by acidified thiosulphate is not due to hydrogen sulphide.

Since trithionic acid on hydrolysis can generate thiosulphate, as do also tetra- and penta-thionic acids, it is not surprising to find that in strongly acid solution trithionic acid slowly bleaches methylene-blue. It is possible that in this case some of the reduction is due to sulphoxylic acid (see p. 1447). The bleaching of the dye took several hundred times longer than in the parallel case with thiosulphate.

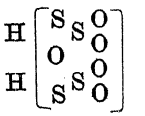
It should be noted that the observation that thiosulphuric acid can bleach indigo and methylene-blue greatly diminishes the value of such bleaching as a test for hydrosulphurous or sulphoxylic acid.

It is also important to realise that *sulphurous acid* is not without action on methylene-blue (and indigo). The strongest solutions (2—3*N*) act upon the methylene-blue or indigo in a similar way to concentrated hydrochloric acid, and very quickly, removing the blue colour and leaving only a pale purple or brown colour. This action, which appears to be due to the formation of addition compounds of acid and dye, falls off rapidly with dilution of the acid, whether this be hydrochloric or sulphurous acid. Even with 10*N*-hydrochloric acid it is only obvious when very little methylene-blue and an enormous excess of acid are used. In the case of sulphurous acid, it seems to be followed by a definite reducing action on the dye; this action is very slow, however, and is under investigation. We have satisfied ourselves that this action of strong hydrochloric acid or of sulphurous acid does not appreciably affect the results which we record in Expts. T and V.

The formation of tetrathionate from thiosulphate by methylene-blue in strongly acid solution furnishes a strong argument against the view that thiosulphuric acid can yield sulphoxylic acid according to the equation $H_2S_2O_3 + H_2O \rightleftharpoons 2S(OH)_2$ (see pp. 1405—6). Since sulphoxylic acid would probably be a very weak acid (like hypochlorous acid), strongly acidic conditions would be just those likely to favour such a change, were it possible. Experiments with sodium formaldehydesulphoxylate showed that, at the ordinary temperature, it bleaches methylene-blue relatively slowly in strongly acid solution, with formation of sulphite only (Expt. V). Were the bleaching action of the strongly acid thiosulphate solutions due to sulphoxylic acid, four times as much methylene-blue should be reduced as is actually observed.

It seems most probable that the acid $H_2S_4O_5$ is formed by the elimination of a molecule of water from two hydroxyl groups, not from one hydroxyl and one thiol group (which would probably give

off a molecule of hydrogen sulphide to yield one form of trithionic acid). In this case it is to be regarded as having the structure



If, and when, either of the hydrogen ions ceases to be ionised, it can become attached by covalencies to either a sulphur or an oxygen atom. Three tautomeric structures are thus possible for the non-ionised $H_2S_4O_5$ just as two are possible for non-ionised thiosulphuric acid. Systematically $H_2S_4O_5$ might be called dithiopyrosulphuric acid.

Action of Sulphurous Acid and Hydrogen Sulphide on Thiosulphate.

Sulphurous acid and hydrogen sulphide are two acids which act upon thiosulphates in rather special ways, owing to their peculiar relationships to thiosulphuric acid and the polythionic acids.

The action of sulphurous acid is to cause the decomposition of thiosulphuric acid to take place much more in accordance with equation (IX). This it does partly by preventing reaction (VIII), of which it is a product, partly by forming the relatively stable, yellow addition compound, $H_2S_2O_3,SO_2$, and partly by removing hydrogen sulphide by reacting with it in accordance with equations (II*b*) and (I*b*). The sulphur resulting from reactions (II*b*) and (I*b*) does not, under favourable conditions, separate as such, but regenerates thiosulphate according to reaction (VIII). It is thus possible to get practically quantitative conversion of thiosulphate into trithionate, *e.g.*, by acting upon a saturated solution of potassium thiosulphate with strong sulphurous acid solutions at 30° (Hertlein, *Z. physikal. Chem.*, 1896, **19**, 292). Under ideal conditions the reactions which occur could be summarised by an equation such as $K_2S_2O_3 + 4SO_2 + H_2O = K_2S_3O_6 + H_2S_3O_6$. Action does not, of course, cease with the formation of trithionate. Continued action of sulphurous acid causes hydrolysis of trithionate, and ultimately sulphate and sulphur appear; tetra- and penta-thionate may be formed in the intermediate stages.

An elaborate investigation of the action of sulphurous acid on thiosulphate has been made recently by Foerster and Vogel (*loc. cit.*).

When hydrogen sulphide is passed into a solution of sodium thiosulphate, precipitation of sulphur occurs, slowly at the ordinary temperature, but more quickly on warming. This is due to decomposition of thiosulphuric acid displaced by the hydrogen sulphide and to the usual interaction of hydrogen sulphide and sulphurous acid (Reactions VIII*a*, II*b*, and I*b*). On heating, the solution

becomes yellow, owing to the formation of polysulphide, and if the passage of hydrogen sulphide is discontinued, the whole of the precipitated sulphur ultimately dissolves. If the solution is boiled for a sufficient time, the yellow colour disappears, and the solution is then, as a rule, alkaline to phenolphthalein. If hydrogen sulphide is again passed in, more sulphur will be precipitated, and will dissolve on heating, and all the above operations can be repeated indefinitely.

During the boiling, all the reactions of decomposition which occurred during the passage of hydrogen sulphide are reversed with regeneration of thiosulphate, but during this period there is a tendency for sodium sulphide and sulphite to produce some free alkali owing to hydrolysis.

The Wackenroder Reaction and the Genesis of the Polythionic Acids.

If equation (II) is accepted as representing the way in which sulphoxylic acid changes into hydrogen sulphide and sulphurous acid, it follows with reasonable certainty that the first step in the interaction of hydrogen sulphide and sulphur dioxide in the Wackenroder reaction is the converse of this change. The first step would thus give sulphoxylic acid and its pyro-derivative, which would then be hydrolysed to sulphoxylic acid. Interaction of the latter with hydrogen sulphide would give rise to sulphur (reaction I*b*). The freshly formed sulphur would be in a very suitable form to react with sulphurous acid to produce thiosulphuric acid (reaction VIII), which, as has been mentioned already, is relatively stable from the point of view of this reaction in dilute, feebly acid solutions. Trithionate will then be formed from thiosulphuric acid according to reaction (IX) (see p. 1417), whilst it is not impossible that some trithionate may be formed in two steps from sulphurous acid and sulphoxylic acid by a reversal of the reactions considered on p. 1447, as has, in fact, been suggested by Foerster and Vogel (*loc. cit.*), who give a reaction $SO + 2HSO_3' \longrightarrow S_3O_6'' + H_2O$. We found that traces of polythionates were formed by shaking sulphurous acid with a solution of sulphur in benzene, whilst, by passing sulphur dioxide and sulphur vapour simultaneously into water, a solution 0·32*N* with respect to sulphurous acid and about 0·01*N* with respect to a mixture of tri- and tetra-thionic acids was obtained.

In the latest paper on the subject (*Z. anorg. Chem.*, 1926, **157**, 80), Foerster and Centner definitely conclude that, in some cases at least, trithionate cannot result from degradation of pentathionate, but must be formed directly. They favour a reaction $S_2O_3'' + 4HSO_3' + 2H^{\cdot} \longrightarrow 2S_3O_6'' + 3H_2O$, which corresponds to that given by us on p. 1440, and which can only be a summation equation.

If reaction (II) really is the first step in the Wackenroder reaction, all the peculiarities of the initial stages of the reaction which were noticed by Debus (J., 1888, **53**, 336) and Riesenfeld and Feld (*Z. anorg. Chem.*, 1921, **119**, 225) can be accounted for just as readily as on the basis of the primary reaction $H_2SO_3 + H_2S \rightleftharpoons H_2SO_2 + H_2SO$, proposed by Heinze (*J. pr. Chem.*, 1919, **99**, 109), or of the reaction $H_2S + 2H_2SO_3 \rightleftharpoons 3\{SO + H_2O\}$ suggested by Riesenfeld and Feld (*loc. cit.*), or that—$H_2S + H_2SO_3 \rightleftharpoons H_2S_2O_2 + H_2O$—put forward by Foerster and Hornig (*loc. cit.*, p. 92). This matter has been considered by Foerster and Hornig (*loc. cit.*, pp. 87—90), and their explanation will suit our reaction as well as either of the above.

Riesenfeld and Feld's reaction is very similar to our reaction (II), since their $\{SO + H_2O\}$ is really sulphoxylic acid, but a termolecular reaction is much less probable than a bimolecular one.

No proof that sulphoxylic acid is a primary product of the Wackenroder reaction is available, but it is extremely probable that the bleaching of indigo by sulphurous acid solutions freshly treated with hydrogen sulphide is, in the main, due to sulphoxylic acid. This bleaching effect was first noted by Spring (*Bull. Acad. roy. Belg.*, 1878, **45**, 605; *op. cit.*, Vol. II, p. 1060), and we have confirmed it, but in view of the fact that thiosulphuric acid also bleaches indigo, methylene-blue, etc., such bleaching can only be regarded as a very uncertain test for either hydrosulphurous or sulphoxylic acid (see p. 1435).

Whilst the primary reaction in the Wackenroder solution is being considered, it may be pointed out that, since dry hydrogen sulphide and sulphur dioxide do not react, it is unlikely that the one is oxidised directly by the other. Even in presence of water vapour the mixed gases seem to be stable and only to react on the surface of the containing vessel—presumably in the film of adsorbed moisture. We have also found that when hydrogen sulphide is passed into liquid sulphur dioxide no interaction occurs; this is contrary to the statement of Quam (*J. Amer. Chem. Soc.*, 1925, **47**, 103), but agrees with Matthews's observations (*loc. cit.*). The mechanism we have suggested for the interaction of these two gases in presence of water cannot, of course, be applied to their interaction in presence of other dry liquids (Matthews, *loc. cit.*). Some complex other than pyrosulphurous acid must be involved in such cases, as suggested by Klein (*J. Physical Chem.*, 1911, **15**, 1).

Pentathionic acid has generally been regarded as the first thionic acid to appear, both in the case of the decomposition of thiosulphates by acids and in the Wackenroder reaction, tetra- and tri-thionic acids being subsequently formed from it by loss of sulphur. Debus

(*loc. cit.*, pp. 339, 344) considered that in both these reactions the anhydride of pentathionic was formed by direct polymerisation of the anhydride of thiosulphuric acid : $5S_2O_2 = 2S_5O_5$, the necessary S_2O_2 being given by the addition of nascent sulphur to sulphur dioxide. In the Wackenroder reaction, some tetrathionic acid was formed directly according to the scheme $3SO_2 + H_2S = H_2S_4O_6$. In both reactions, he believed that tetra- and tri-thionic acids resulted from degradation of pentathionic acid.

All recent workers on polythionates seem to follow Debus, although there are several variants of the condensation which is supposed to produce pentathionic acid. Raschig ("Schwefel- und Stickstoff-Studien," 1924, pp. 273—304) assumes the polymerisation of S_2O_2 to $S_{10}O_{10}$, which gives pentathionic acid *via* the hypothetical $H_4S_{10}O_{12}$. Riesenfeld and Feld (*loc. cit.*, p. 252) assume that SO is first formed and gives S_5O_5 by polymerisation and thence pentathionic acid by hydration. Foerster and Hornig (*loc. cit.*) suggest an eleventh-order ionic variant of the above polymerisation, $5S_2O_3'' + 6H^{\cdot} \longrightarrow 2S_5O_6'' + 3H_2O$, and this appears to be accepted by the most recent workers in this field, Kurtenacker and Kaufmann (*loc. cit.*, p. 256).

Arithmetically, such polymerisations as the above are simple enough, and this seems to be the chief argument which has led to the suggestion that pentathionic is the first-formed thionic acid. Kinetically, the matter is very different, however, and the polymerisation could only occur in a series of steps. This difficulty has been realised by Foerster and Vogel (*loc. cit.*, p. 163), who now suggest that pentathionic acid is formed by a reaction $SO + 2HS_2O_3' \longrightarrow S_5O_6'' + H_2O$.

We have found that the first thionic acid to appear during the decomposition of thiosulphate by acids is trithionic, although it is generally accompanied by some tetrathionic. It is true that pentathionic acid may appear after a very short time, especially under drastic conditions (see p. 1433). All the observations made in this section of our work make it almost certain that pentathionic acid is the last to be formed, not the first, whilst the experiments and arguments brought forward up to this point are most in favour of the view that trithionic acid is the first to be formed (Expt. W).

When hydrogen sulphide and sulphurous acid interact in dilute solution, we also find that trithionic acid is the first thionic acid to appear, and we think there can be no doubt that, in the Wackenroder reaction also, tetra- and penta-thionic acids are built up from trithionic acid (Expt. X).

The Structural Formulæ of the Polythionates and their Hydrolysis in Acid and in Alkaline Solution.

Dithionic acid is not considered in this paper, as it is not formed under the conditions which give rise to the other thionic acids. The structure and mode of hydrolysis of trithionic acid have already been dealt with on pp. 1421, 1422.

Tetrathionic Acid.—The formation of tetrathionates from thiosulphates by oxidation leads naturally to the structure

$$OH{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}SO_2{\cdot}OH$$

for tetrathionic acid, whilst the ease with which one atom of sulphur is removed from tetrathionate by sulphite to yield trithionate and thiosulphate (Colefax, J., 1908, **93**, 798) supports the structure $OH{\cdot}SO_2{\cdot}S(\cdot S){\cdot}SO_2{\cdot}OH$. A study of the solid model suggests that the two formulæ are probably equally correct in the sense that the slight electronic adjustment needed for one form to pass into the other appears to offer no insuperable difficulty.

Pentathionic Acid.—For this acid the structure $OH{\cdot}SO_2{\cdot}\overset{\overset{S}{|}}{S}{\cdot}SO_2{\cdot}OH$ seems definitely preferable to the alternative $OH{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}S{\cdot}SO_2{\cdot}OH$. The chief arguments in its favour are (i) its compactness and symmetry, (ii) 3 of the 5 sulphur atoms have a co-ordination number of four, (iii) 2 atoms of sulphur are readily removed by sulphite to yield trithionate. The thionic acid formulæ with all the sulphur atoms in one straight chain were originally suggested by Mendeléev (*J. Russ. Phys. Chem. Soc.*, 1870, **2**, 276; 1871, **3**, 871), and they have been more or less accepted ever since, although it has been recognised that the evidence in support was slender.

Formulæ for sodium tri-, tetra-, and penta-thionates have been proposed by Raschig (*op. cit.*, p. 305), but there seems to be nothing in their favour and much against them. Martin and Metz (*Z. anorg. Chem.*, 1923, **127**, 91) also have proposed formulæ for the polythionates.

Many of the objections to the chain formulæ have been summarised by Vogel (J., 1925, **127**, 2248), who suggested the structures $OH{\cdot}SO_2{\cdot}S(\cdot S){\cdot}SO_2{\cdot}OH$ and $(OH{\cdot}SO_2)_2{:}S{\cdot}S{\cdot}S$ for tetra- and pentathionic acids, respectively. With this formula for tetrathionic acid, tautomeric with the chain formula, we agree, but we consider that our formula for pentathionic acid is preferable to Vogel's, for the reasons given above.

In our opinion, it is the tendency of the central sulphur atom in trithionic acid to become co-ordinated with four other atoms in all, which is the prime cause of the readiness with which tetra- and

penta-thionic acids are built up from trithionic. This building-up process comes more or less to an end with the symmetrical pentathionate, and on these grounds the existence of hexathionic acid is improbable. It is true that Debus (*loc. cit.*, pp. 301—309) thought he had some evidence for hexathionates, but no later worker has prepared either hexathionic acid or hexathionates. Higher polythionates than pentathionate only seem likely if the two central sulphur atoms in the straight-chain form of tetrathionic acid can add on additional sulphur atoms in the same way as does the one central sulphur atom of trithionic acid. The building-up process in this case would come to an end with octathionic acid,

$$OH{\cdot}SO_2{\cdot}\overset{\overset{S}{|}}{\underset{\underset{S}{|}}{S}}{\cdot}\overset{\overset{S}{|}}{\underset{\underset{S}{|}}{S}}{\cdot}SO_2{\cdot}OH,$$

with hexa- and hepta-thionic acids as intermediate stages. We have some experiments in progress which seem to suggest that this is actually possible.

The reactions of the polythionates are essentially reactions of hydrolysis and decomposition, and the formulæ proposed above offer a satisfactory explanation of all the facts observed. The hydrolysis of tri-, tetra-, and penta-thionic acids has been the subject of careful investigations by Foerster and Hornig (*loc. cit.*, p. 86) and by Kurtenacker and Kaufmann (*loc. cit.*, pp. 43, 369). Some of the difficulties which arise in connexion with the hydrolysis of trithionic acid have been dealt with on pp. 1421, 1422.

The nature of this hydrolysis is of importance in relation to that of tetra- and penta-thionic acids, for trithionic acid is invariably formed when they are hydrolysed. This seems to occur either by direct decomposition according to the reactions (XII*b*) and (XIII*b*), and perhaps $H_2S_5O_6 \rightleftharpoons H_2S_3O_6 + S_2$, or else by the intervention of sulphurous and thiosulphuric acids, which are products of the hydrolysis of trithionic acid, in accordance with the reactions (XIV), (XV), and (VIII).

In view of what has been stated on p. 1428 in connexion with reaction (VIII), it is very probable that the decomposition of penta- and tetra-thionic acids in accordance with reactions (XII) and (XIII) really follows a bimolecular course, and that the equations should therefore be doubled so as to indicate the formation of S_2 units.

The final products of acid hydrolysis of tri-, tetra-, or pentathionic acid are sulphuric acid, sulphur dioxide, and sulphur, a small quantity of hydrogen sulphide being formed in the intermediate stages. Kessler (*loc. cit.*) alludes to this formation of hydrogen sulphide, and we have noticed that it is always produced.

Under strongly alkaline conditions, the final result of hydrolysis can be represented by the equations

$$2H_2S_3O_6 + 3H_2O \rightleftarrows H_2S_2O_3 + 4H_2SO_3 \quad . \quad . \quad . \quad (a)$$
$$2H_2S_4O_6 + 3H_2O \rightleftarrows 3H_2S_2O_3 + 2H_2SO_3 \quad . \quad . \quad . \quad (b)$$
$$2H_2S_5O_6 + 3H_2O \rightleftarrows 5H_2S_2O_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

(Kurtenacker and Kaufmann, *loc. cit.*, p. 369), but in the case of tetra- and penta-thionates, the tri- and tetra-thionates are formed to some extent as intermediate steps, and in absence of sufficient hydroxyl-ion concentration some hydrolysis of trithionate in the manner characteristic of acid conditions occurs, with consequent formation of sulphate (see p. 1422).

In considering the above results, we wish to stress two important governing factors: (i) Tri-, tetra-, and penta-thionic acids are all of the nature of pyro- or anhydro-acids, and so would be expected to break up in alkaline solution or on dilution, and to be relatively more stable the more acid the solution. Complications are introduced by the instability of the products of hydrolysis, thiosulphuric and sulphurous acids, but the general correctness of these deductions is illustrated by the great difficulty in preparing pentathionates, owing to the readiness with which they decompose, although in strongly acid solution, pentathionic acid is the most stable of the three acids. (ii) The tendency for a sulphur atom to become co-ordinated with four other atoms is the second governing factor.

Equations (*a*), (*b*), and (*c*) above are only to be regarded as summation equations, but if we consider them for a moment as representing directly reversible reactions, and bearing in mind that thiosulphuric and tri-, tetra-, and penta-thionic acids are all strong acids, whilst sulphurous acid is much weaker, we see that the formation of pentathionic acid according to equation (*c*) would correspond to a much greater decrease of acidity than would the formation of either tri- or tetra-thionic acid according to equation (*a*) or (*b*). This is probably a main reason for the greater stability of penta-thionic acid in acid solution, and its great instability under alkaline conditions.

In discussing the relative stability of compounds, it is most important to realise that this cannot be done in general terms, but only with reference to specified conditions—a matter which is frequently overlooked. Vogel's general statement (*loc. cit.*) that the relative stabilities of the polythionic acids should decrease in the order di-, tri-, tetra-, and penta- has no meaning, nor has Foerster and Centner's statement (*loc. cit.*, p. 56) that pentathionate is much less stable than tetrathionate.

The hydrolysis of the unsymmetrical form of trithionic acid has been dealt with on p. 1421, but the mechanism of the hydrolysis of the symmetrical form, which finally yields sulphite and thiosulphate, has not been considered. Since no sulphate is formed, it seems clear that in the first step the hydroxyl group becomes attached to the central sulphur atom, and not to a terminal one, yielding a molecule of sulphonic acid and an unstable intermediate compound which is to be regarded as thiopermonosulphuric acid :

$$\begin{matrix} OH\cdot SO_2 \\ H \end{matrix}\!\!\begin{matrix} \vdots \\ \vdots \end{matrix}\!\!\begin{matrix} S\cdot SO_2\cdot OH \\ OH \end{matrix} \longrightarrow H\cdot SO_3H + OH\cdot S\cdot SO_2\cdot OH$$

Further hydrolysis of the thiopermonosulphuric acid yields sulphoxylic acid and another molecule of sulphonic acid: $OH\cdot S\cdot SO_2\cdot OH + H_2O \longrightarrow S(OH)_2 + H\cdot SO_3H$. The sulphoxylic acid is then oxidised to sulphurous acid by another molecule of thiopermonosulphuric acid which is itself reduced to thiosulphate : $S(OH)_2 + OH\cdot S\cdot SO_2\cdot OH \longrightarrow H_2SO_3 + H_2S_2O_3$. The final result of the hydrolysis in alkaline solution is represented by equation (*a*) on p. 1446.

If this picture of the mechanism of the hydrolysis is correct, it should be possible to produce trithionate from sulphoxylic and sulphurous (sulphonic) acids. We attempted such a synthesis by boiling a solution of sodium formaldehydesulphoxylate (1 mol.) and sodium pyrosulphite (1½ mols.), but were unable to obtain any definite or conclusive results.

The hydrolysis of tetra- and penta-thionic acids is explicable along similar lines. The fact that pentathionate on treatment with sodium carbonate loses one atom of sulphur to form tetrathionate (Raschig, *op. cit.*, pp. 273—304), not two to form trithionate, suggests that in alkaline solution tetrathionate has the straight-chain structure, although it would seem to pass readily into the other form, $OH\cdot SO_2\cdot S(\cdot S)\cdot SO_2\cdot OH$, since sulphite converts it into trithionate. Hydrolysis of the straight-chain form would yield 1 mol. of thiosulphate and 1 mol. of thiopermonosulphuric acid, which would then give rise to thiosulphate and sulphite, as already indicated. Complete alkaline hydrolysis of tetrathionate would thus take place in accordance with equation (*b*) on p. 1446.

In the case of pentathionic acid, the sulphur atom dropped in the very first step of all (equation XIII) suffices to convert a molecule of sulphite into thiosulphate, so that in this case complete alkaline hydrolysis yields nothing but thiosulphate [equation (*c*), p. 1446].

Acid hydrolysis of pentathionic acid may be expected to follow a different course. If the hydroxyl group becomes attached to the central sulphur atom, as in the case of trithionic acid, the first step would yield an intermediate product which can be regarded as

dithiodithionic acid. This would, no doubt, be very unstable and might be expected to break up into sulphur and thiopermono-

$$OH{\cdot}SO_2{\cdot}S(:S_2){\cdot}SO_2{\cdot}OH \xrightarrow{H_2O} \underset{\text{sulphonic acid}}{H{\cdot}SO_2{\cdot}OH} + \underset{\text{dithiodithionic acid}}{OH{\cdot}S(:S_2){\cdot}SO_2{\cdot}OH}$$

sulphuric acid, which would then react further as indicated on p. 1447. It is possible that an intermediate compound $OH{\cdot}S(\cdot S){\cdot}SO_2{\cdot}OH$ might similarly be formed by acid hydrolysis of the unsymmetrical form of tetrathionic acid, $OH{\cdot}SO_2{\cdot}S(\cdot S){\cdot}SO_2{\cdot}OH$.

The influence of hydrogen-ion concentration on the relative stability of tri-, tetra-, and penta-thionic acids is not easy to forecast in any detailed manner. Reactions (XII) and (XIII) will only be dependent upon hydrogen-ion concentration in so far as the relative strengths of the three acids differ. Precise information on the strengths of these acids is lacking, although we know that they are all strong acids.

The strength might be expected to diminish in the order penta-, tetra-, tri-, in view of the fact that the content of "negative" sulphur diminishes in this order. If this is correct, decrease of acidity should tend to favour reactions (XII*a*) and (XIII*a*). The accepted statements (Debus, Raschig, *locc. cit.*) that alkali causes the formation of tetrathionate and sulphur from pentathionate, however, contradict this. It follows therefore that, either pentathionic acid is the weakest of the three acids, which is possible, or else that its decomposition into tetrathionic acid and sulphur is only apparent—that is to say, reaction (XIII*b*) does not occur directly at all, but only as the final result of a more or less complex series of changes [*e.g.*, slight hydrolysis in conjunction with reactions (XV*b*) and (VIII*a*)], some part of which is definitely favoured by decrease of acidity. In any case it is certain that the proportions of tri-, tetra-, and penta-thionic acids which can exist in a solution depend, among other things, upon the hydrogen-ion concentration, increase and decrease of which favour the formation of penta- and tri-thionic acid, respectively. The effect of change of acidity is so great that the separation of sulphur on addition of alkali is almost as delicate a test for pentathionate as is the ammoniacal silver nitrate test.

Experimental.

Expt. A. (Theory, p. 1403.)—Solutions containing known amounts of sodium formaldehydesulphoxylate, sodium hydroxide, and lead acetate were heated to boiling for a short time and allowed to cool. The mixture of lead sulphide and metallic lead was filtered off and

washed, finally with alcohol, dried as quickly as possible at 100°, and weighed. It was then converted into lead sulphate and weighed again. The following results were obtained in three experiments :

	I.	II.	III.
Sodium formaldehydesulphoxylate (g.) ...	2·4	2·4	1·2
N/2-Lead acetate (c.c.)	5	5	5
2*N*-Sodium hydroxide (c.c.)	10	2	10
Molecular ratio, Pb/PbS, in precipitate ...	1·82	2·27	2·69

Sufficient water was added in the second and third experiments to make the total volume the same as that of the mixture used in the first experiment. The sodium formaldehydesulphoxylate used in this and following experiments had the composition NaCl, 10; Na_2SO_4,10H_2O, 6·1; Na_2CO_3,10H_2O, 21·1; CH_3O_3SNa, 62·8%. Chloride, sulphate, sulphoxylate, and total sodium were estimated, and carbonate (proved qualitatively) was calculated. The sulphoxylate was determined by the methods of Helwig (*Amer. Dyestuff Reporter*, 1920, **7**, ii, 12) and Hollingsworth Smith (*J. Amer. Chem. Soc.*, 1921, **43**, 1307), which gave the same results.

Expt. B. (Theory, p. 1405.)—A bright silver coin (92·5% Ag) was digested for 1 hour with sulphur, 1 c.c. of 0·3*N*-potassium dichromate, 1 c.c. of 2*N*-phosphoric acid, and about 20 c.c. of water. Very little sulphide attached itself to the coin; most remained mixed with the sulphur.

Loss of weight of coin = 0·0079 g.
Ag_2S produced = 0·0078 g.
Sulphate formed, as $BaSO_4$ = 0·0063 g.
} Molecular ratio, $Ag_2S : BaSO_4 = 1·17$.

Expt. C. (Theory, p. 1405.)—10 C.c. of a solution containing 0·2 g. of the sodium formaldehydesulphoxylate (= 0·1256 g. pure sulphoxylate) were mixed with 10 c.c. of 2*N*-sodium hydroxide, 5 c.c. of 0·5*N*-lead acetate, and 5 c.c. of 2*N*-barium chloride. After simmering for ½ hour in an atmosphere of purified coal gas, the mixture of lead sulphide, metallic lead, and barium sulphate was filtered off. The lead and lead sulphide were extracted with warm dilute hydrochloric acid, and the barium sulphate was weighed; 0·0146 g. was obtained, of which 0·0088 g. was due to sulphate present in the sulphoxylate used. Decomposition of sulphoxylate in accordance with a reaction $2H_2SO_2 \longrightarrow H_2S + H_2SO_4$ would yield 0·1242 g. of barium sulphate; 0·0058 g. is only 4·6% of this, and no importance can be attached to it.

Expt. D. (Theory, pp. 1403, 1405.)—(I) 20 C.c. of 1·25*N*-hydrochloric acid containing 0·315 g. of pure sulphoxylate were digested for 80 mins. in a small flask connected to two wash-bottles containing

N/10-iodine and a third containing N/40-thiosulphate. A slow current of purified coal gas passed through the apparatus. The iodine reduced was 82% of that required by a reaction $2H_2SO_2 \longrightarrow S + H_2SO_3 + H_2O$, which is a combination of reactions (I) and (II). After the precipitated sulphur had been filtered off, any sulphate formed during the decomposition was precipitated and weighed as barium sulphate; only 0·0163 g. was obtained, and as 0·022 g. was to be expected from the sulphate present in the sulphoxylate used, it is clear that no sulphate had been formed during the hydrolysis. The filtrate from the barium sulphate gave a reaction for pentathionate, and the formation of this and other thionic acids would account for only 82% of the calculated amount of sulphurous acid being obtained. The weight of sulphur precipitated in this experiment was difficult to estimate exactly owing to the presence of some trithioformaldehyde, but it also corresponded to about 82% of that demanded by the above equation. Another experiment, similar to the above, in which some lead acetate was added to the reacting solution gave practically identical results. No metallic lead or lead sulphide was precipitated and 0·0185 g. of barium sulphate was obtained.

(II) 10 C.c. of sulphoxylate solution (= 1 g. crude or 0·628 g. pure sulphoxylate), 20 c.c. of 1% arsenious oxide solution, and 10 c.c. of concentrated hydrochloric acid were boiled in a current of purified coal gas until the arsenious sulphide had coagulated, and then for a further 15 mins. to drive out sulphur dioxide. The sulphide was filtered off and weighed. The filtrate after considerable dilution and treatment with barium nitrate gave a very small precipitate of barium sulphate on standing [Found: As_2S_3, 0·1444 g. Calc. (from the weight of sulphoxylate used on the basis of reaction II): 0·1447 g. Found: $BaSO_4$, 0·0226 g. Calc. (for sulphate present in the sulphoxylate used): 0·044 g.].

Expt. E. (Theory, p. 1405.)—To a mixture of 20 c.c. of 1% arsenious oxide solution and 10 c.c. of concentrated hydrochloric acid were added 2 c.c. of 2N-thiosulphate. After the mixture had been boiled to expel sulphur dioxide, the precipitate, which consisted mainly of arsenious sulphide, was filtered off and weighed. Sulphate in the diluted filtrate was precipitated as barium sulphate (Found: As_2S_3, 0·0654 g.; $BaSO_4$, 0·3908 g.).

Expt. F. (Theory, p. 1408.)—100 C.c. of a solution containing 1·2289 g. of sodium hydrosulphite (of 88·7% purity) and 0·3750 g. of sodium carbonate were left exposed to the air at room temperature, and the unoxidised hydrosulphite was determined at intervals by Hollingsworth Smith's method (*loc. cit.*): k is the value of the expression $1/t \cdot \log_e a/(a - x)$.

t (mins.).	% $Na_2S_2O_4$ present.	$k \times 10^4$.	t (mins.).	% $Na_2S_2O_4$ present.	$k \times 10^4$.
0	88·7	—	80	54·9	60·0
10	82·4	73·4	140	39·4	58·1
20	80·6	47·8	260	16·5	64·8
40	69·6	60·9			

The rate of oxidation and the actual value of k will depend on the exact conditions of exposure, which were, however, approximately constant during the experiment.

Expt. G. (Theory, p. 1414.)—Analyses are given in Table I of a number of old sulphurous acid solutions, none of which had deposited any visible sulphur. Sulphurous and sulphuric acids were determined by iodine titration followed by estimation of total sulphate. Polythionic acids were estimated in a separate portion, from which sulphur dioxide had been expelled either by boiling or by means of an air current.

The method we have used for analysing mixtures of polythionic acids depends on one of the tests given by Takamatzu and Smith (J., 1880, **37**, 608), *viz.*, the addition of silver nitrate to the neutral or acid solution. The general reaction may be expressed $Ag_2S_xO_6 \longrightarrow Ag_2S + (x - 3)S + 2SO_3$, whence the molecular ratios of silver sulphide to free atomic sulphur precipitated are, for trithionate 1 : 0, for tetrathionate 1 : 1, and for pentathionate 1 : 2. Since colloidal and precipitated sulphur react slowly with silver nitrate to form silver sulphide, a standard solution of silver nitrate should be used in only very slight excess. Decomposition of the silver polythionates is rapid at temperatures near 100°, so it is best to heat the solution nearly to this temperature before adding the silver nitrate. The silver sulphide–sulphur precipitate, which filters easily, is well washed, finally with ammonia or ammonium carbonate solution. (This is to remove sulphuric acid, which otherwise is obstinately retained and causes charring of the filter paper on drying.) The precipitate is dried at 100° and weighed. A portion is then weighed into a glass ignition tube and heated until all free sulphur (if present) is driven off. Brilliant, black, crystalline silver sulphide remains and is weighed. This method, although simple and expeditious, gives surprisingly reproducible results, whilst it enables the presence of very small amounts of free sulphur to be detected with certainty owing to the dark colour of the distillate. Although the ratio Ag_2S : S may be found to be 1 : 1, this does not prove the presence of pure tetrathionate unless it has been shown that pentathionate is absent, which can be most readily done by the well-known ammoniacal silver nitrate test.

It is to be noted that after sulphur dioxide had been expelled by an air current at the ordinary temperature, both tri- and tetra-

TABLE I.

Age of solution.	6 months.	1 year.	1¾ years.	2·5 years.	5 years.	12 years.
Original normality.	High, but not recorded.	Not recorded.	1·141	0·2688	High, but not recorded.	0·0996
Final normality :						
H_2SO_3	0·975	0·0855	0·567	0·055	0·0515	0·0680
H_2SO_4	0·201	0·0122	0·0542	0·0821	0·412	0·0236
$H_2S_3O_6$ } After boiling	—	0·0038	0·0005	0·0002	0·0101	0·0021
$H_2S_4O_6$ } off SO_2.	—	—	0·0013	—	—	—
$H_2S_2O_3$ } After displac-	—	—	0·0056	—	—	—
$H_2S_3O_6$ } ing SO_2 with	0·0002	—	—	—	0·0037	0·0011
$H_2S_4O_6$ } air current.	—	—	—	—	0·0029	0·0005
Remarks (based on known conditions of storage).	Mostly atmospheric oxidation.	Little, if any, atmospheric oxidation.		Much SO_2 had escaped through rubber tube and probably some atmospheric oxidation had occurred.	Much atmospheric oxidation known to have occurred.	Little, if any atmospheric oxidation.

TABLE IV.

The Hydrolysis of Potassium Trithionate in Neutral and in Acid Solution at Room Temperature.

(Calculated for 100 millimols. of $K_2S_3O_6$.)

		S_2O_6''.	S_4O_6''.	S_5O_6''.	S_2O_3''.	HSO_3'.	SO_4'' developed.	S deposit.	Total S content (Theory, 300).	Acidity = $H^{\cdot}$ developed owing to hydrolysis.	Conditions of expt.		
											Normality of $K_2S_3O_6$.	Time (days).	Solvent.
i.	(K. & K.)	44·5	25·0	0	6·5	27·2	31·5	0	305·2	41·3	0·184	28	Water
ii.	(B. & D.)	35·0	23·7	0	0	34·0	51·1	14·1	299·1	35·4	0·1	42	0·1*N*-H_2SO_4
iii.	(K. & K.)	9·8	30·0	0	0	73·0	54·0	26·7	305·2	27·0	0·184	28	*N*-HCl
iv.	(B. & D.)	0	19·3	1·6	0	56·4	105·6	57·0	303·3	98·0	0·05	280	0·05*N*-H_2SO_4

thionic acids were present, but after the sulphur dioxide had been boiled off only trithionic acid was found. We satisfied ourselves that these sulphurous acid solutions contained neither colloidal sulphur, thiosulphate, nor pentathionate. Only the $1\frac{3}{4}$-year old solution seemed definitely to contain thiosulphate. After the sulphur dioxide had been boiled off, both tri- and tetra-thionic acids were found in this case.

Expt. H. (Theory, p. 1416.)—Table II epitomises a series of experiments in which solutions of the concentrations stated were boiled for 2 minutes in a small conical flask, 20 c.c. being used in each experiment. Hydrochloric acid was used. The mouth of the flask was covered with a filter paper moistened in the centre with one drop of 2*N*-lead acetate solution. The stains of lead sulphide produced were compared and preserved.

In the more concentrated thiosulphate solutions, sulphur dioxide was evolved as well as hydrogen sulphide, which accounts for the fact that the latter appears to reach a maximum with *N*/100-acids, as shown in cols. 2, 3, and 4 of the table. Although the two gases can coexist in gaseous mixtures for considerable periods of time, lead acetate is not darkened when sulphur dioxide is largely in excess. The non-appearance of hydrogen sulphide under the conditions represented above the sloping line suggests that its production is due to a molecular rather than to an ionic reaction.

TABLE II.

Acid normality.	*N*-$Na_2S_2O_3$.	0·1*N*-$Na_2S_2O_3$.	0·01*N*-$Na_2S_2O_3$.	0·001*N*-$Na_2S_2O_3$.	0·0001*N*-$Na_2S_2O_3$.
1×10^{-7} (= H_2O)	H_2Sf, 0				
5×10^{-7}	H_2Sf, 0				
5×10^{-6}	H_2Sf, 0				
5×10^{-5}	H_2Sf, 0	H_2Sf, Ⓢ			
5×10^{-4}	H_2S, Ⓢ	H_2S, Ⓢ	H_2Sf, 0		
1×10^{-3}	H_2S, Ⓢ	H_2S, Ⓢ	H_2S, S		
5×10^{-3}	H_2S, Ⓢ	H_2S, S	H_2S, S		
1×10^{-2}	$\boxed{H_2S}$, S	$\boxed{H_2S}$, S	$\boxed{H_2S}$, S		
5×10^{-2}	$\boxed{H_2S}$, S	H_2Sf, S	H_2S, S	H_2Sf, 0	
5×10^{-1}	H_2Sf, S	S	H_2S, S	H_2S, 0	H_2Sf, 0
5	$\boxed{S}$.	$\boxed{S}$	H_2S, S	$\boxed{H_2S}$, 0	$\boxed{H_2S}$, 0

Abbreviations:

0, no sulphur separated.

Ⓢ, sulphur appeared and later disappeared.

S, sulphur was permanently precipitated.

$\boxed{S}$ or $\boxed{H_2S}$, the substance appeared to have reached a maximum in respect to the *vertical column*.

H_2Sf, a *faint* stain due to hydrogen sulphide.

Expt. I.—(i) (Theory, p. 1418). 5·86 G. of hydrated sodium thiosulphate, 1 c.c. of 0·2*N*-sodium hydroxide, and 5 c.c. of water were boiled for 5 mins. and cooled; addition of sodium plumbite then gave an immediate brown coloration.

(ii) (Theory, p. 1418). 20 C.c. of an aqueous solution containing 1·4 g. of hydrated sodium thiosulphate and 20 c.c. of 2*N*-sodium hydroxide were heated to boiling for 50 mins. in an atmosphere of purified coal gas, then acidified with hydrochloric acid and boiled in coal gas to decompose thiosulphate and drive off sulphur dioxide. Sulphate present in the solution was then estimated as barium sulphate: 0·0030 g. was obtained (mean of three experiments) after subtracting (α) the barium sulphate (0·0020 g.) due to sulphate formed during the decomposition of the thiosulphate with acid, and (β) sulphate, silicate, etc. (0·0083 g.), derived from the action of alkali on the glass. Both corrections were determined separately.

A similar solution after boiling for 50 mins. in coal gas was treated with 5 c.c. of 0·5*N*-lead acetate solution. This gave an immediate brown colour, and after short heating lead sulphide coagulated and was weighed as sulphate. In another experiment the lead acetate was added before the boiling with alkali. The two results were identical (Found: $PbSO_4$, 0·0443 g.). This lead sulphate represents sulphide formed by reaction (IX), but corresponds to only 5·8% of the original thiosulphate. The sulphate also formed is derived from the hydrolysis of a small proportion of the trithionate formed in the main reaction.

(iii) (Theory, p. 1419). 1·4 G. of hydrated sodium thiosulphate, dissolved in 20 c.c. of 8·4*N*-caustic soda and boiled for 50 mins. in coal gas, gave the merest trace of sulphide on treatment with lead acetate. On large dilution with water no further precipitate appeared.

(iv) (Theory, p. 1419). 10 C.c. of 2*N*-caustic soda, 2·5 c.c of 2*N*-sodium sulphite, and 20 c.c. of 0·0072*N*-hydrogen sulphide were digested in coal gas for 1 hour at the b. p.; 1 c.c. of 0·5*N*-lead acetate solution was then added. An immediate black precipitate was formed which was filtered off and weighed as lead sulphate. A blank experiment using 2·5 c.c. of water instead of the sodium sulphite was also carried out (Found, from sulphite mixture: $PbSO_4$, 0·0273 g.; from blank: $PbSO_4$, 0·0260 g.).

(v) (Theory, p. 1419). 20 C.c. of 2*N*-caustic soda, 5 c.c. of 2*N*-sodium sulphite, and 1 c.c. each of 2*N*-sodium thiosulphate and 2*N*-sodium sulphide were boiled for 50 mins. in coal gas, and then treated with 5 c.c. of 0·5*N*-lead acetate. The lead sulphide precipitated was converted into 0·2886 g. of sulphate, whereas a blank experiment without sulphite and thiosulphate gave 0·2903 g.

(vi) (Theory, p. 1418). This experiment was similar to the last, but 2 c.c. of 2*N*-sodium sulphate were used instead of the sulphite, and double the quantity of thiosulphate (*i.e.*, 2 c.c.) was used; 0·2885 g. of lead sulphate was obtained, again showing that no disappearance of sulphide had occurred during the boiling. Some thiosulphate was added, as it was thought that, if sulphide would not act directly on the sulphate, it might possibly react with thiosulphate to form trithionate, which would then react with the sulphide to form thiosulphate.

We could get no indication of any thiosulphate formation when hydrogen sulphide was allowed to act upon sodium sulphate either at the ordinary temperature or at 100°. Numerous experiments were made under various conditions of concentration, etc.

(vii) (Theory, p. 1418). 0·2988 G. of lead thiosulphate was boiled with 20 c.c. of 2*N*-sodium hydroxide, in which it dissolved, in an atmosphere of hydrogen. There was no trace of darkening or precipitate after 50 mins'. boiling. 0·8250 G. of lead thiosulphate, when boiled in hydrogen with 25·9 c.c. of 0·2*N*-sodium hydroxide (*i.e.*, the equivalent amount of alkali), became cream-coloured, but showed no sign of sulphide formation after 10 mins'. boiling.

When lead thiosulphate is boiled with less than the equivalent amount of alkali, decomposition is rapid and large amounts of trithionate are obtained, but a considerable proportion of the trithionate is decomposed into sulphide and sulphate, with consequent neutralisation of the alkali used—in fact, the reaction mixture becomes slightly acid. The black precipitate obtained was shown to be a mixture of lead sulphide and sulphate with sometimes a little unaltered thiosulphate, a trace of which may also remain in the solution. The filtrate from the lead sulphide and sulphate precipitate was analysed for thiosulphate and trithionate, one portion being titrated with *N*/100-iodine, and the trithionate and thiosulphate in another portion being obtained from the weight of silver sulphide given on treatment with silver nitrate. The results of two such experiments are given in Table III.

TABLE III.

	I.	II.
PbS_2O_3 (g.)	0·9012	0·7126
H_2O (c.c.)	10	10
NaOH	1 c.c. 2*N*.	5 c.c. 0·2*N*.
Ag_2S from trithionate (g.)	0·1680	0·1507
Ag_2S from thiosulphate (g.)	0·0135	0·0163

In both experiments, the mixture was boiled for 5 mins. in an atmosphere of hydrogen. In the second experiment, the mixture was left over-night after the boiling before filtering.

(viii) (Theory, p. 1418). Even under weakly acid conditions, some trithionate can survive during the decomposition of lead thiosulphate: 1·3974 g. of lead thiosulphate, 5 c.c. of 2·175*N*-acetic acid, and 20 c.c. of water were boiled for 5 mins.; sulphur dioxide was given off, and the black residue contained considerable free sulphur. The filtrate contained trithionate capable of giving with silver nitrate 0·0897 g. of silver sulphide, and thiosulphate equivalent to 0·0368 g. of silver sulphide (the thiosulphate was obtained by titration with *N*/100-iodine—some sulphurous acid may have been present, in which case the value for trithionate would be correspondingly greater).

Expt. J. (Theory, p. 1420.)—Freshly precipitated and washed manganese sulphide, obtained from the hydrated sulphate, was gently boiled in a narrow-mouthed, conical flask, closed by a funnel, with a solution of 10 g. of ammonium sulphate in about 50 c.c. of water, until all the sulphide had reacted, *i.e.*, for 3—5 hours. In Expts. I, III, and IV, 1·1 g. of $MnSO_4,4H_2O$ was used; in Expt. II, 2·2 g. Hydrogen was passed through the flask in which Expt. IV was carried out, but even so, indications of yellow ammonium sulphide were seen at the end of the exit tube inside the flask—a sign of slight oxidation. The sulphide used in Expt. I had undergone more oxidation during its preparation than the other samples. The filtrates from the small amounts of higher oxide of manganese (very small in Expt. III) were analysed by titrating one portion with *N*/100-iodine, and weighing the silver sulphide obtained with silver nitrate from another portion. The silver sulphide was shown to contain no free sulphur, and in amount it agreed very closely with that required by the iodine titration, showing that it was derived from thiosulphate, not trithionate:

	I.	II.	III.	IV.
Ag_2S weighed (g.)	0·1290	0·0662	0·0144	0·0048
Ag_2S calc. from iodine titration	(Not titrated.)	0·0669	0·0139	0·0050

A series of experiments in which hydrogen sulphide was passed through boiling strong solutions of ammonium magnesium and ammonium nickel sulphates gave entirely negative results, no trithionate or thiosulphate being formed.

Expt. K. (Theory, p. 1421.)—The following is a typical experiment: Hydrogen sulphide was passed through a mixture of 5 c.c. of concentrated sulphuric acid and 3 c.c. of water for 70 mins. No sulphur was precipitated. The gas was then displaced from the solution by a very rapid current of hydrogen, and the solution was diluted rapidly to 100 c.c.; this caused an immediate opalescence due to sulphur. Some of the diluted solution, when tested with

ammoniacal silver nitrate, gave a faint coloration such as would be expected from the sulphur cloud; the paleness indicated that all the hydrogen sulphide had been removed. The silver sulphide from half of the solution amounted to 0·0029 g. and the $N/100$-iodine titration indicated that one-third was derived from trithionate and two-thirds from thiosulphate. The cloud of sulphur formed on dilution is attributed to formation and decomposition of thiosulphate owing to the large addition of water having caused hydrolysis of trithionic acid originally present. In other experiments, it was noted that traces of hydrogen sulphide continued to be removed by the current of hydrogen from the original strong acid after several hours. This suggests a slow reversal of reaction (X) by the water present. The thiosulphate found in the solutions after dilution had probably been formed by hydrolysis from trithionate, partly during the removal of hydrogen sulphide by the current of hydrogen, and partly during the dilution.

Expt. L. (Theory, p. 1423.)—0·4884 G. of potassium trithionate and 20 c.c. of $5N$-hydrochloric acid were gradually heated to boiling. Sulphur appeared at about 50°. Boiling was continued until no more sulphur dioxide was liberated—about 25 mins. in all. The liberated sulphur weighed 0·0335 g. and a further 0·0032 g. separated on dilution owing to decomposition of pentathionic acid. This small quantity was filtered off after being boiled for 1 hour to cause coagulation. Sulphate present in the filtrate gave 0·4817 g. of barium sulphate, whereas if 1 mol. of trithionate gave 1 mol. of sulphate, the weight would have been 0·4216 g.

Expt. M. (Theory, p. 1423.)—Potassium trithionate solutions of the concentrations given in Table IV (p. 1452) were left at room temperature for the stated periods and then analysed. Our polythionate estimations (B. and D.) were made by the silver nitrate method (see Expt. G), whereas Kurtenacker and Kaufmann (K. and K.) used volumetric methods.

It is evident that N-hydrochloric acid had hastened the hydrolysis to a later stage in 28 days than had $N/10$-sulphuric acid in 42 days. Obviously our experiment (iv) represents the latest stage of the four —again confirming our contention that pentathionic acid is the last polythionic acid to be produced. Kurtenacker and Kaufmann also expected this, but had not reached it in (iii).

Expt. N. (Theory, p. 1425.)—Four mixtures of sodium thiosulphate and hydrochloric acid of the composition stated in Table V, (i), (ii), (iii), and (iv) were made by adding 1 c.c. of M-sodium thiosulphate to 10 c.c. or 21 c.c. of hydrochloric acid of appropriate strength in small, tightly-corked flasks. After the stated intervals of time, the whole mixture was titrated with $N/10$-iodine, a separate

TABLE V.

Extension of Holleman's Experiments.

(*a*) 0·5*M*-$Na_2S_2O_3 = a$; 1·0*N*-HCl.

t.	*N*/10-Iodine, c.c.	$BaSO_4$ (g.).	*x.*	*x* (alternative calc.).	*k.*
0·5	11·95	0·0611	0·165	0·154	1·97
1	12·8	0·0816	0·210	0·221	1·45
2	13·9	0·1097	0·276	0·308	1·23
4	14·35	0·1316	0·348	0·343	1·15
5	14·6	0·1381	0·363	0·363	1·06
6	14·5	0·1416	0·383		
7	14·2	0·1432	0·410		
43 hrs.	10·25				

(*b*) 0·25*M*-$Na_2S_2O_3 = a$; 0·5*N*-HCl.

1	12·1	0·0528	0·060	0·121	1·26
2	13·2	0·0895	0·113	0·147	1·65
5	13·9	0·1217	0·153	0·225	1·59
10	14·0	0·1462	0·215	0·231	2·46
15	14·1	0·1541	0·228	0·237	2·75
20	14·2	0·1615	0·243	0·243	6·94
30	13·8	0·1623			
240	12·6	0·1750			
43 hrs.	9·75				

(*c*) 0·1*M*-$Na_2S_2O_3 = a$; 0·2*N*-HCl.

t.	*N*/10-Iodine, c.c.	*x.*	*k.*
0·5	10·5	0·0091	2·00
1	10·7	0·0128	1·47
5	11·9	0·0347	1·06
10	12·8	0·0511	1·02
15	13·1	0·0566	0·87
17	13·2	0·0584	0·83
18	13·1	58·4% Decomposed at 17 mins. according to sulphate estimation after the iodine titration.	
20	12·7		
25	11·9		
30	11·7		
43 hrs.	9·25		

(i) 0·0455*M*-$Na_2S_2O_3 = a$; 0·196*M*-HCl.

t.	*N*/10-Iodine (c.c.).	*x.*	*k.*
1	10·5	0·00437	2·33
3	10·9	0·00785	1·53
5	11·2	0·0105	1·32
7	11·8	0·0158	1·66
10	11·95	0·0176	1·32
15	12·6	0·0228	1·47
20	13·13	0·0274	1·66
30	13·7	0·0324	(2·70)
40	14·2	0·0368	(2·31)
60	14·8	0·0420	(4·39)
80	15·1	0·0446	(13·62)
120	15·2	—	—
		Mean	1·61

Limiting val. used for calc., 15·2.

(ii) 0·0455*M*-$Na_2S_2O_3 = a$; 0·393*M*-HCl.

t.	*N*/10-Iodine (c.c.).	*x.*	*k.*
1	10·55	0·00463	2·49
3	11·0	0·00842	1·66
5	11·4	0·0118	1·54
7	11·85	0·0156	1·64
10	12·4	0·0202	1·76
15	12·85	0·0240	1·64
20	13·6	0·0303	2·19
30	14·5	0·0379	(3·65)
		Mean	1·85

Limiting val. used for calc., 15·4.

TABLE V. (*contd.*)

(iii) 0·091*M*-$Na_2S_2O_3$ = *a*; 0·393*M*-HCl.

t.	*N*/10-Iodine (c.c.).	*x.*	*k.*
1	10·9	0·0152	2·20
5	12·4	0·0404	1·76
10	13·4	0·0573	1·87
15	14·1	0·0691	2·31
20	14·3	0·0725	2·15
35	14·6	0·0775	1·81
40	14·85	0·0817	(2·42)
60	15·4		
80	15·2		
120	15·1		

Mean 2·02

Limiting val. used for calc., 15·4.

(iv) 0·091*M*-$Na_2S_2O_3$ = *a*; 1·96*M*-HCl.

t.	*N*/10-Iodine (c.c.).	*x.*	*k.*
1	11·5	0·0182	2·75
3	13·1	0·0376	2·58
5	14·0	0·0485	2·51
7	14·6	0·0546	2·36
10	15·3	0·0643	2·65
15	15·7	0·0692	2·33
20	16·3	0·0764	2·88
30	17·0	0·0849	(5·10)
40	17·3	0·0886	(10·14)
60	17·4	0·0898	(13·74)
80	—		
120	17·2		

Mean 2·58

Limiting val. used for calc., 17·5.

mixture being used for each titration. The amount of iodine required at zero time was, of course, 10 c.c. in each case. In these experiments, since excess of acid was used, it can be safely assumed that decomposition of thiosulphate was complete when the iodine titration had reached its limiting value. The amount of decomposition at earlier stages was calculated by simple proportion. Holleman's three experiments, in which equivalent amounts of thiosulphate and acid were used, were also repeated (Expts. *a*, *b*, and *c*). At the time stated, a known quantity of *N*/10-iodine was added and the excess was then titrated with *N*/10-thiosulphate. After 1 min. we obtained similar results to his, but we followed up the experiments in order to determine the maximum values of the titre so that the velocity coefficient might be calculated in the manner indicated on p. 1428. For this purpose, the sulphate present in the titrated solution was also determined. In experiments (*a*) and (*b*) the sulphate was determined at each stage (and is given in the table as g. of barium sulphate) in order to get a direct measure of the amount of decomposition to compare with that calculated by simple proportion from the iodine titre and the sulphate formed at the stage of maximum iodine titre.

In all these experiments, which were carried out at 17°, the initial concentrations shown are those which obtained after mixing. Time, *t*, is given in minutes, unless otherwise stated. The number of mols. of thiosulphate decomposed is given by *x*; and *k* is the bimolecular velocity coefficient calculated from $k = x/ta(a - x)$.

Expt. O. (Theory, p. 1430; Fig. 1.)—Mixtures were made of 1 c.c. of 0·05, 0·1, 0·25, 0·5, or 1·0*M*-sodium thiosulphate with 10 c.c. of hydrochloric acid (or, in the cases indicated, phosphoric acid) of the *molecular* normalities shown on the abscissæ of Fig. 1, where the results are given in the form of curves. As ordinates are plotted

the times (in mins.) required for the first appearance of visible sulphur, which could not, of course, be determined with very great accuracy. The actual normalities of thiosulphate and of acid in the mixture would be 10/11ths of those indicated. The experiments were done at room temperature (about 17°).

Expt. P. (Theory, p. 1432.)—Four separate mixtures were made, each containing 1 c.c. of each of the specified constituents: (1) 0·1*M*-Thiosulphate, 0·5*N*-hydrochloric acid, water: Sulphur deposition began 90 secs. after mixing. (2) 0·1*M*-Thiosulphate, 0·5*M*-potassium tetrathionate, 0·5*N*-hydrochloric acid: This remained absolutely clear for 24 hours after mixing. It then gave a strong reaction for pentathionate. The original tetrathionate contained only a faint trace of pentathionate. (3) 0·5*M*-Thiosulphate, 0·5*M*-sulphuric acid, water: Sulphur deposition started in 15 secs. and was soon very heavy. (4) 0·5*M*-Thiosulphate, 0·5*M*-potassium tetrathionate, 0·5*M*-sulphuric acid: Faint sulphur deposit after 2 mins. It was only slight after 10 mins. Concentrations are stated in molecular normalities in all cases. Since we made these experiments, similar ones have been recorded by Foerster and Centner (*loc. cit.*, pp. 64, 68).

Expt. Q. (Theory, p. 1432.)—0·203 G. of iodine in 20 c.c. of alcohol was mixed with 0·216 g. of potassium trithionate in 20 c.c. of water, and hydrogen sulphide was then passed in very slowly until the iodine was decolorised. Some sulphur was deposited, which was filtered off, washed, dried, and found to weigh 0·0153 g. To the filtrate was added 0·265 g. of lead nitrate in 20 c.c. of water. After standing for 5 hours, the lead iodide was filtered off and washed once. The filtrate from this iodide was warmed with 5 c.c. of 0·4*N*-silver nitrate and the precipitated mixture of silver sulphide and iodide and free sulphur was dried, weighed, and gently heated in an ignition tube. In this way it was found to contain 0·0104 g. of free sulphur. It represents the tetrathionate formed by direct addition of sulphur. The iodine used in the experiment would have liberated 0·0256 g. of sulphur, so that 40·6% was absorbed. In a second experiment using twice as much trithionate, 60·2% of the sulphur was absorbed.

Expt. R. (Theory, p. 1434.)—One c.c. of 0·05*M*-sodium thiosulphate and 10 c.c. of 0·25*N*-hydrochloric acid gave a deposit of sulphur in 9½ mins. When this mixture was neutralised by caustic soda after 7 mins., no precipitation of sulphur occurred either then or after ½ hour. In a second experiment, 1 c.c. of lanthanum nitrate solution was added after 7 mins., but no precipitate occurred until after 13 mins. On the other hand, neutralisation of the above mixture after 9 mins. caused an immediate opalescence and so also did addition of 1 c.c. of lanthanum nitrate solution after 9 mins.

When 1 c.c. of 0·1*M*-thiosulphate and 10 c.c. of 0·25*N*-hydrochloric acid were used, sulphur separated 5 mins. after acidification. Similar mixtures were neutralised with sodium hydroxide 2 mins. and 3 mins. after acidification. No sulphur had separated after an hour, but a precipitate formed when the neutralisation was effected after 4 or 4½ mins.

One c.c. of 0·1*M*-thiosulphate and 10 c.c. of 2·163*N*-hydrochloric acid deposited sulphur in 4 mins. 10 secs. To a similar mixture, 3 c.c. of 8*N*-caustic soda were added 3 mins. after acidification. An immediate opalescence was produced. This faded and disappeared after 2 mins. The solution was finally alkaline. One c.c. of 0·1*M*-thiosulphate and 10 c.c. of 5*N*-hydrochloric acid gave a deposit of sulphur in 15 mins. A similar mixture was carefully neutralised with 8*N*-caustic soda in presence of phenolphthalein within a few minutes of preparation. No immediate precipitation of sulphur occurred, but a faint opalescence appeared 13½ mins. from the start, and disappeared after a further minute. A somewhat similar result was obtained with 0·5*M*-thiosulphate and 5*N*-hydrochloric acid.

Expt. S. (Theory, p. 1435.)—In the following experiments 1 c.c. of *M*-thiosulphate and 10 c.c. of 10·5*N*-hydrochloric acid were mixed. (In the first experiment, 10 c.c. of 9*N*-acid were used.) The mixtures were left at room temperature for the times specified (in Table VI) in tightly-corked, small flasks. They were then titrated with 0·1*N*-iodine. In the first four experiments this was done in the concentrated mixture, without using starch and in presence of the precipitated sodium chloride. In the case of Expts. 2, 3, and 4, owing to the large amount of sulphurous acid present, the yellow iodide–sulphur dioxide complex was formed. Addition of a little water towards the end of the titration broke this down and enabled the end-point to be determined sharply. The solutions were then raised to boiling point to coagulate sulphur, which was filtered off and weighed. The filtrate was diluted considerably and reheated, and sulphate present was precipitated and weighed as barium sulphate. This sulphate is due to oxidation of sulphurous acid by iodine, but may be partly due to hydrolysis of thionic acids during the heating, etc. In Expt. 5 the solution was diluted with 50 c.c. of water before being titrated with iodine.

TABLE VI.

Expt.	Time elapsed before titration.	*N*/10-Iodine (c.c.).	$BaSO_4$ (g.).	Sulphur deposited (g.).
1	10 mins.	12·5	0·0714	—
2	2 hours	12·1	0·1082	0·0206
3	21 ,,	11·1	0·1559	0·0290
4	23·5 ,,	10·7	0·1663	0·0326
5	23·5 ,,	10·2	0·1175	0·0242

In the mixture used in Expt. 1, sulphur began to appear after 11 min. 50 sec.; some was seen just before the end of the titration with iodine. In the other experiments, most of the sulphur separated during the titration (owing to the consequent dilution) and subsequent heating, indicating that it originated from pentathionate.

If we assume that the reduction of iodine is due to sulphurous acid and thiosulphuric acid (or $H_2S_4O_5$) only, we can make the following deductions. In Expt. 1, 63·7% of thiosulphuric acid had remained unchanged (as $H_2S_4O_5$, in our opinion), and 30·6% had decomposed according to reaction (VIII). This assumes that all the barium sulphate had resulted from sulphurous acid and that no hydrolysis of polythionate had occurred. In Expt. 2, again assuming no hydrolysis of polythionate, 28·3% of thiosulphuric acid (as $H_2S_4O_5$) had remained, whilst 46·4% had decomposed according to reaction (VIII).

In Expts. 3, 4, and 5 it appears that no thiosulphuric acid remained in the cold solution, and if that is correct, the determinations show that: (α) In (3), 55·5% had decomposed according to reaction (VIII), and none remained undecomposed. Of the polythionate present in the cold mixture an amount corresponding to 0·0264 g. of barium sulphate had been decomposed during the boiling.

(β) In (4) and (5), 53·5% and 51%, respectively, had decomposed according to reaction (VIII). In (5), the barium sulphate obtained was equivalent to the iodine used, showing that no hydrolysis of polythionate had occurred during the boiling of the diluted solution; but in (4), where the boiling lasted longer than in (3), polythionate corresponding to 0·0414 g. of barium sulphate had been decomposed.

It should be noted that actually more thiosulphuric acid will have decomposed according to reaction (VIII) than is shown by the residual sulphurous acid, for some of the latter will have reacted with hydrogen sulphide, formed by reaction (IX), to yield sulphur (reactions II*b* and I*b*). The amount of thiosulphuric acid which has reacted to form polythionate cannot therefore be obtained by deducting from the original amount that remaining undecomposed and that which has decomposed in accordance with reaction (VIII).

Expt. T. (Theory, p. 1436.)—(i) An aqueous solution of methylene-blue was prepared containing 0·64 g. per litre (= 1/500th g.-mol. $C_{16}H_{18}N_3SCl$). One c.c. of 0·1*M*-sodium thiosulphate was added to 10 c.c. of hydrochloric acid, which was either 10*N*, 5*N*, or 2·5*N*. With each strength of acid two mixtures were made. To one, 24·5 c.c. of the methylene-blue solution were added, and to the other 25·5 c.c., the mixtures being in tightly-corked flasks filled with carbon dioxide. In each case, the solutions containing 24·5 c.c.

of methylene-blue were bleached, whilst those containing 25·5 c.c. retained a pale blue colour. The thiosulphate used in the experiment could reduce 25 c.c. of the methylene-blue solution according to the equation given on p. 1435.

Another bleaching experiment was done in a slightly different way, using a solution which was 0·1*M* with respect to thiosulphuric acid without any excess of other acid, obtained by mixing equal volumes of 0·2*M*-sodium thiosulphate and 0·4*M*-hydrochloric acid; on shaking this solution with solid methylene-blue in an atmosphere of carbon dioxide, it was found to bleach exactly the amount calculated from the equation, but no more.

0·32 G. of methylene-blue was dissolved in 100 c.c. of water and the solution placed in a separating funnel filled with carbon dioxide; 2 c.c. of *M*-sodium thiosulphate were added, followed by 10 c.c. of 2·5*N*-hydrochloric acid. The mixture was well shaken, and the colour disappeared completely in ½ hour; 9·84 c.c. of 2·564*N*-sodium hydroxide were then added, this being the amount required to produce neutrality after due allowance for the fact that 1 mol. of hydrochloric acid is liberated from methylene-blue for each mol. of the *leuco*-compound produced, whilst, on the other hand, each mol. of tetrathionate formed corresponds to the neutralisation of 2 mols. of hydrochloric acid. Immediately on addition of the alkali a white, flocculent precipitate was thrown out, which dissolved at once in ether. The ethereal extract was separated and the ether distilled in a current of carbon dioxide, leaving the *leuco*-methylene-blue as long, colourless crystals. These do not melt, but decompose on heating. They slowly turn blue owing to oxidation. The *leuco*-compound is strongly basic and cannot be extracted from acid solution by ether, although it is freely soluble in absence of acid. Bernthsen (*Ber.*, 1883, **16**, 1025; *Annalen*, 1885, **230**, 147) prepared it by reduction of methylene-blue with hydrosulphite ($Na_2S_2O_4$) followed by ether extraction.

Expt. U. (Theory, p. 1437.)—The times taken for the disappearance of the blue colour from mixtures of thiosulphate, hydrochloric acid, and methylene-blue were carefully noted, the thiosulphate being added last of all and the timing starting from then. These times are given (in secs.) under *t* in Table VII; they are the average of two or more concordant readings and are subject to an experimental error of at least 5%. The temperature was 15° throughout, and the same weight of methylene-blue (*viz.*, 0·0064 g.) was used in each experiment.

The total volume in each experiment was 21 c.c., 1 c.c. of *N*-, 0·5*N*-, or 0·2*N*-thiosulphate being added to 20 c.c. of 10*N*-, 5*N*-, 2·5*N*-, 1·25*N*-, 0·625*N*-, or 0·5*N*-hydrochloric acid containing the

methylene-blue. The resulting normalities are shown in the table. (In this experiment, $N = \frac{1}{2}M$ for thiosulphate.)

TABLE VII.

Times of disappearance of colour from 0·0064 *g. of methylene-blue in solutions containing thiosulphate and hydrochloric acid of concentrations given in horizontal and vertical columns, respectively.*

	Conc. of HCl.	Column 1. 0·0476*N*-$H_2S_2O_3$. *t.*	Column 2. 0·0238*N*-$H_2S_2O_3$. *t.*	Column 3. 0·00952*N*-$H_2S_2O_3$. *t.*
a.	9·50*N*	41	104	450
b.	4·75*N*	20·3	61·4	250
c.	2·38*N*	21·6	61·8	265
d.	1·19*N*	37	117	840
e.	0·594*N*	78	230	1740
f.	0·475*N*	90	330	2160

The amounts of thiosulphate used in columns 1, 2, and 3 are, respectively, 8, 16, and 40%, since 0·0064 g. of methylene-blue has been shown to react with 40% of the weight of thiosulphate in column 3.

Aqueous solutions of methylene-blue can be kept without change of concentration or behaviour for more than a year. The solutions in 10*N*- and in 5*N*-hydrochloric acid, when freshly made, react with thiosulphate to give colourless solutions, but if they are kept for 3 days before mixing with thiosulphate, the reaction ceases before the solution is colourless, a green tint remaining. Dilute solutions of hydrochloric acid will dissolve only a portion of the methylene-blue, even although left for many days. All experiments with concentrations lower than 10*N*-hydrochloric acid were carried out by mixing an aqueous solution with appropriate amounts of acid just before the start, and usually it was found that no "salting out" of methylene-blue occurred in the short time the experiment lasted. When "salting out" does occur, it may begin soon after the addition of thiosulphate, and if so the experiment must be started afresh.

The following table gives the figures in Expts. *d*, *e*, and *f* (of Table VII) relatively to the 37-minute value for *d* 1, which is taken as unity, on the assumption that the variations are inversely as the square of the thiosulphate concentrations and also as the first power of the hydrochloric acid concentrations.

	(1.)	Theory.	Ratios.	(2).	Theory.	Ratios.	(3).	Theory.
d.	1	1	(1)	3·16	4	(1)	22·7	25
e.	2·108	2	(2·14)	6·75	8	(2·07)	47·0	50
f.	2·43	2·5	(2·82)	8·93	10	(2·56)	58·3	62·5

Expt. V. (Theory, p. 1439.)—One c.c. of 0·0628*M*-sodium formaldehydesulphoxylate was added to 10 c.c. of 10*N*-hydrochloric acid,

and the times taken to bleach successive amounts of a methylene-blue solution containing 0·00064 g. per c.c. were noted. The sulphoxylate should have been able to bleach 31·4 c.c. of the methylene-blue if oxidation gave sulphite alone.

25 C.c. were bleached in 133 mins.; 27 c.c. (total) were bleached in 172 mins.; 29 c.c. (total) in 215 mins.; 31 c.c. (total) in 285 mins.; 33 c.c. (total) in 415 mins. The reaction was then complete.

Expt. W. (Theory, p. 1443.)—Polythionic acids were formed in thiosulphate solutions which had been acidified under varying conditions. The polythionates were not estimated individually, but on the basis of the S/Ag_2S ratio, as explained in Expt. G. Before the polythionates can be satisfactorily determined by this method, it is necessary to remove sulphurous acid or to render it inactive towards silver nitrate. In most cases this was done by boiling, which, unfortunately, has two undesirable effects: some polythionate is hydrolysed, and at the same time higher polythionates are formed at the expense of lower ones. These two effects are the more pronounced the greater the acidity of the solutions.

In a few experiments formaldehyde was added (compare Kurtenacker and Bittner, *Z. anorg. Chem.*, 1924, **141**, 297). This enables the polythionates to be determined directly by the silver nitrate method without any previous boiling. In another case, sulphur dioxide was removed by means of a brisk air current before the silver nitrate reaction was carried out.

When considered collectively, the experiments recorded in Table VIII show that trithionic acid is formed in the earlier stages of the decomposition, but that time, acidity, and boiling all tend to shift the balance in favour of pentathionic acid.

In Table VIII the columns numbered I—IX are given by the following key:

I. Normality of thiosulphate (*i.e.*, referred to $\frac{1}{2}Na_2S_2O_3$).
II. Nature and normality of acid used (referred to $1H_3PO_4$ or $\frac{1}{2}H_2SO_4$).
III. Precipitated sulphur (mg.).
IV. Silver sulphide (mg.).
V. Mg. of sulphur mixed with silver sulphide.
VI. Molecular ratio, S/Ag_2S.
VII. Molecular ratio of trithionate to tetrathionate (taken as 100).
VIII. „ „ „ pentathionate „ „ „ „.
IX. Ratio of sulphur, %, in polythionate to that in original thiosulphate.

Expt. X. (Theory, p. 1443.)—Solutions of sulphurous acid and hydrogen sulphide of known strength were prepared. Mixtures of

TABLE VIII.

Experimental results.					*Calculations from experiments.*				
I	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	Observations.
0·5	0·513*N*-Phosphoric acid.	121·9	147·2	9·1	0·479	108	—	20·6	Boiled for 20 mins. immediately after mixing.
„		110·5	179·1	18·9	0·819	32	—	27·5	Left for 23 hours; then boiled for 20 mins.
„		126·7	183·5	11·5	0·485	106	—	25·8	Mixed slowly, acid added in 11 stages in 30 mins., then boiled for 20 mins.
„		123·4	195·5	10·7	0·424	136	—	27·0	Mixed slowly, thiosulphate added in 11 stages, then boiled for 20 mins.
„		104·3	214·1	25·1	0·909	10	—	35·0	Acid and thiosulphate left to mix by diffusion for 45 hours, then boiled for 20 mins.
„		93·7	333·3	32·1	0·747	34	—	50·3	Acid and thiosulphate left to mix by diffusion for 214 hours, then boiled for 20 mins.
	1·5*N*-Phosphoric acid.	134·8	46·6	8·4	1·363	—	57	8·25	Boiled for 20 mins. immediately after mixing.
„*		133·1	53·9	8·3	1·193	—	24	9·1	Boiled for 20 mins. immediately after mixing.
„		131·6	52·9	10·0	1·465	—	85	9·5	Left for 23 hours; then boiled for 20 mins.
„		131·6	50·8	9·8	1·495	—	93	9·2	Mixed slowly, acid added in 11 stages in 30 mins., then boiled for 20 mins.
„		86·0	235·0	41·0	1·352	—	54	41·2	Acid and thiosulphate left to mix by diffusion for 45 hours, then boiled for 20 mins.
„		88·0	249·5	41·7	1·295	—	42	43·2	Acid and thiosulphate left to mix by diffusion for 216 hours, then boiled for 20 mins.
„	0·55*N* Sulphuric acid (isohydric with 1·5*N*-H_3PO_4).	133·6	58·5	8·8	1·165	—	20	9·8	Boiled for 20 mins. immediately after mixing.
„		123·4	87·5	14·6	1·324	—	48	15·1	Left for 23 hours and then boiled for 20 mins.
„		110·8	166·2	28·3	1·319	—	47	29·9	Mixed and left for 45 hours, then boiled for 20 mins.
„		123·4	71·9	10·8	1·164	—	20	12·1	Mixed slowly, acid added in 11 stages in 30 mins., then boiled for 20 mins.
„		114·6	192·3	29·4	1·178	—	22	32·4	Acid and thiosulphate left to mix by diffusion for 45 hours, then boiled for 20 mins.
„		105·3	249·4	36·1	1·122	—	44	41·0	Acid and thiosulphate left to mix by diffusion for 216 hours, then boiled for 20 mins.
„		6·2	124·8	4·0	0·243	311	—	16·8	Excess of formalin added immediately after mixing; no boiling.†
„		97·4	321·3	17·6	0·424	135	—	44·4	Excess of formalin added after 5 hours' standing; no boiling.
„		126·5	128·6	17·4	1·049	—	5	21·0	Excess of formalin added after 23 hours' standing; no boiling.
„		116·0	179·0	12·7	0·553	81	—	25·6	SO_2 removed by brisk current of air bubbled through for 1¼ hours directly after mixing; no boiling.
0·16	1·4*N* Acetic acid.	65·8	31·5	2·8	0·396	152	—	4·7	Left at room temperature for 37 hours, then kept simmering for 1 hour. 30% of thiosulphate remained. The calculation is for the 70% decomposed.
0·5	0·52*N*	56·2	6·9	0·6	0·678	47·5	—	1·0	Kept at about 75° for 24 hours, boiled for 20 mins. 64% of thiosulphate remained. The calculation is for the 36% decomposed.
0·33‡	2·8‡	155·7	212·3	15·0	0·735	36	—	29·3	Result of a 5-hour distillation, 10 c.c. *N*-$Na_2S_2O_3$ with 40 c.c. 4·25*N*-acetic acid. Considerable hydrolysis with formation of H_2SO_4 occurred. Total sulphur in all products estimated, good sulphur balance obtained. 15% of thiosulphate remained. The calculation is for the 85% decomposed.

* In this experiment the phosphoric acid was 1·2*N*.

† The formalin stopped the reaction. Only 20% of the thiosulphate had been decomposed (iodine titration). The figures refer to this 20%. The iodine titration of thiosulphate in presence of formalin takes a considerable time (Schmidt, *Ber.*, 1907, **40**, 865).

‡ These normalities represent approximate average—acetic acid distilled over and hydrogen sulphide was evolved continuously. The volume of the solution in the distillation flask was kept approximately constant by the slow addition of 4·25*N*-acetic acid.

TABLE IX.

The Interaction of Solutions of H_2SO_3 and H_2S in Various Concentrations and Proportions, and for Various Times.

Normalities when mixed, H_2SO_3.	Normalities when mixed, H_2S.	Molar ratio, SO_2/H_2S.	S ppt. in cold.	S ppt. on heating.	No. of c.c. used.	Duration of action.	From polythionic acid (g). Ag_2S	From polythionic acid (g). S	$S/Ag_2S = r$.	% of polythionate produced (referred to H_2S employed).	Remarks.
0·0323	0·00375	8·4	Slight cloud, none ppd.		100	10 hrs.	Small amount.	0	0		The figures in the last column are calculated on the basis of a reaction $H_2S + 8SO_2 + 2H_2O = 3H_2S_3O_6$ and the assumption that $3Ag_2S$ would be obtained by the $AgNO_3$ reaction for each H_2S converted to polythionate.
0·0728	0·0028	26	Faint cloud after 15 mins. Clear in 23 hours.	None.	100	23 ,,	0·0172	0	0	16·6	
0·227	0·0088	26	Cloud persists for 40 hours.	None.	30	40 ,,	0·0209	0·0019	0·704	21	The whole mixture, including the cloud of precipitated sulphur, was boiled. There was complete disappearance of S on boiling due to formation of $H_2S_4O_6$ *while boiling.* ($r = 0·704$ gives $H_2S_3O_6 : H_2S_4O_6 = 0·42 : 1$.)
0·227	0·0073	31	Cloud.	None.	50	10 days	0·0517	0	0	37·9	Only the clear solution boiled in this case.
0·235	0·0106	22	Heavier cloud.		100	1 day	0·0451	0·0029	0·5	13·72	Total volume, 280 c.c.; *final deposit of* S *after* 12 *days* = only 0·0342 g. In this set of experiments evidence was obtained to show that no H_2SO_4 is produced in the original action before heating (to drive off excess of SO_2); also by means of iodine added to the *cold* solution and subsequent treatment with $AgNO_3$ it was *proved* that *neither* $H_2S_2O_3$ *nor* $H_2S_4O_6$ was in the *cold* solution after 10 days, since the precipitate consisted only of AgI and Ag_2S without any free sulphur. The $H_2S_4O_6$ is produced during the process of boiling. The *amount* of polythionate from *tri-* upwards increases with *time.*
0·235	0·0106	22	Deposit.	Sulphur cloud appeared after boiling some time.	20	10 days	0·0149	0·0011	0·572	18·91	
0·235	0·0106	22	Total wt. = 0·0342 g. (in 280 c.c.).	A *small* deposit, not weighed.	100	12 ,,	0·0393	0·0040	0·459	22·7	
1·25	0·0205	61	Cloud (total wt. = 0·0240 g.).	A deposit = 0·0128 g. on *total.*	200	6 ,,	0·1966	0·0185	0·729	12·8	No pentathionic acid was present in original *cold* solution.
1·41	0·0113	124	0·0302 g.	0·0156 g.	300	12 ,,	0·1087	0·0101	0·725	8·6	The yield of polythionate is less than before, whilst r is higher.
0·0235	0·0205	1·1	0·0621 g.	0·0013 g.	200	14 ,,	0·0818	0·0058	0·545	5·4	This mixture in ratio for reaction $5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O$ *gave no trace of pentathionate.* The solution after 14 days was still clouded. The S deposited was much *higher,* and the conversion into polythionate *lower,* than in any previous experiment.

these in different proportions were made and kept in tightly-corked flasks for various times. Excess of sulphur dioxide and hydrogen sulphide was then removed by boiling, and the polythionic acids present were estimated by the silver nitrate reaction (Table IX).

Summary.

(1) The hydrolysis of sulphur probably occurs in accordance with the equation $S_2 + 2H_2O \rightleftharpoons H_2S + (HO)_2S$.

(2) Sulphoxylic acid is very unstable either in acid or in alkaline solution, and readily yields hydrogen sulphide and sulphurous acid. The mechanism of this change and its bearing on the initial step in the Wackenroder reaction are discussed.

(3) The cause of the yellow colour of certain simple sulphur compounds is attributed to the presence of a sulphur atom with a ten-electron sheath.

(4) The decomposition of hydrosulphurous acid, $H_2S_2O_4$, is discussed.

(5) The autoxidation of sulphurous acid is considered.

(6) The main part of the paper deals with the decomposition of thiosulphuric acid, and it is shown that this decomposition can occur in three different ways.

(7) One mode of decomposition yields hydrogen sulphide and trithionic acid. This is considered to be an essential step in the Wackenroder reaction also, and trithionic acid is regarded as the primary thionic acid both in the thiosulphate decomposition and in the Wackenroder reaction.

(8) The objections to the usual view that pentathionic acid is the primary thionic acid are dealt with.

(9) It is shown that, in all probability, thiosulphates never decompose directly into sulphide and sulphate, but that the sulphate results from trithionate formed first of all.

(10) Experiments are recorded which suggest that the decomposition of thiosulphuric acid into sulphurous acid and sulphur is probably a bimolecular reaction involving a sulphur unit S_2.

(11) A new mode of decomposition of thiosulphuric acid into an anhydro-acid, $H_2S_4O_5$, is described. The new acid reduces methylene-blue and is thereby oxidised to tetrathionic acid.

(12) The structural formulæ of the polythionic acids and their behaviour on hydrolysis have been considered, and some new points of view put forward.

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CXCVIII.—*The Reaction between Manganese Salts and Sodium Hypochlorite in the Presence of certain other Salts.*

By Bertram Eastwood Dixon and John Ledger White.

From a solution of a manganese salt sodium hypochlorite precipitates hydrated manganese dioxide, and, on prolonged boiling, a small quantity of sodium manganate or permanganate is formed. If the reaction takes place in the presence of copper salts, however, the copper is precipitated and permanganate is the main product. The latter reaction was studied by Duyk (*Ann. Chim. anal.*, 1907, **12**, 465), who gave no data, but stated that the reaction was complete for small quantities of manganese. Heslinga (*Chem. Weekblad*, 1922, **19**, 274) used bromine water in alkaline solution in place of hypochlorite, and stated that the reaction was suitable for qualitative purposes only.

It has been found that a small amount of sodium permanganate is formed even when special precautions are taken to purify both the manganese salt and the sodium hypochlorite, so the manganese dioxide itself appears to be capable of catalysing the reaction. When present in quantities roughly equivalent to that of the manganese salt, the salts of several metals, notably copper, cobalt, nickel, and molybdenum (as molybdate), possess the property of greatly increasing the amount of permanganate formed in this reaction, and the present communication is a study of the effect of variations in the conditions of the experiment on the conversion of manganese salt into permanganate.

Experimental.

Influence of Time.—Of the oxygen available from the hypochlorite, some is utilised in the formation of permanganate, whilst the bulk is evolved as gas. The relations were observed between time of heating, permanganate formation, and evolution of gas at a temperature of 100°.

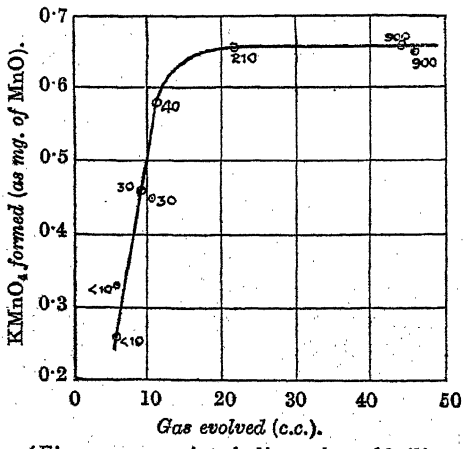
The reactants were mixed at 100° by sharply shaking a small tube, which contained measured amounts of manganese- and copper-salt solutions, and which stood normally in an upright position inside the reaction tube containing the hypochlorite. After being heated for a definite time, the reaction tube was immersed in an ice-bath, the volume of gas evolved was measured, and the permanganate estimated colorimetrically. Only at 100° is the suspension of copper oxide sufficiently agitated, without the use of a stirrer, to exert a constant and maximum influence on the reaction. But since the

reaction has been chiefly studied at this temperature, no attempt has been made to carry out the above experiment at any other temperature. The results were as follows, *all weights of manganese salts and permanganates being expressed, both here and later, as mg. of* MnO:

Time of boiling (secs.)	<10	<10	30	30	40	210	900	900
Volume of gas (c.c.)...	5·4	5·4	10·7	9·4	11·2	21·7	43·8	45·6
$KMnO_4$.....	0·26	0·33	0·45	0·46	0·58	0·66	0·66	0·65

These results are shown graphically in Fig. 1, and it is evident that, at these concentrations, the maximum amount of permanganate is formed at the end of about 3 minutes' boiling, and after the evolution of one-third of the total oxygen.

FIG. 1.



(*Figures near points indicate time of boiling in seconds.*)

Effect of Alkali.—On filtering the above reaction mixtures, it was noticed that the solutions sometimes had a slight bluish tint which made colorimetric comparison with permanganate solution impossible. This was very marked when the bulk of the hypochlorite had been decomposed and the ratio of alkali to hypochlorite had greatly increased. On keeping indefinitely, the solution turned greenish-blue in colour, and a brown precipitate formed. When the filtrate from this solution was treated with acid, the original pink colour was restored, with co-precipitation of manganese dioxide. The colour was found to be due to the formation of a little manganate by the action of sodium hydroxide on the permanganate.

Heslinga (*loc. cit.*) stated that the presence of iron was prejudicial to the reaction, since it caused the colour of the solution to change to bluish-violet, probably through the formation of unstable potassium ferrate. It was found, however, that (1) the bluish-violet colour was observed when no iron was present, (2) this colour formed more readily as the concentration of alkali increased, and (3) the brown precipitate contained manganese, but no iron.

Of the reagents usually employed to convert manganate to permanganate, sodium bicarbonate was found to be the only one

suitable in this case, provided that sufficient hypochlorite was also present.

Extent of Reaction.—Another series of tests was carried out to discover how far the oxidation of the manganese to permanganate was quantitative, starting with different quantities of reactants.

Approximately equivalent measured amounts of manganese and of cobalt or copper salt were poured into a conical flask, and the solution was diluted to 50 c.c. To the warm solution, 10 c.c. of 5*N*-sodium hypochlorite (total alkalinity 0·1*N*) were added gradually, the flask being shaken simultaneously, and the mixture was heated. After reaching brisk effervescence, the solution was boiled for 3 minutes, a further 5 c.c. of hypochlorite were added, and the solution was again heated until it effervesced freely. After filtration through pure asbestos, the solution was cooled, made up to a known volume, and estimated colorimetrically.

I. $KMnO_4$ calc.	0·36	0·73	1·46	2·05	2·19	2·55	2·92	3·66	4·38
II. $KMnO_4$ formed :									
A. Using cobalt.	0·30	0·45	0·91		1·25		1·42		1·80
	0·30	0·46	0·93				1·44		
		0·45					1·47		
B. Using copper.		0·73	1·33	1·64	1·62	2·21	2·39	3·00	3·83
				2·00	1·87	2·50	2·58	3·06	
					2·21	2·50			
					1·98				

From the results obtained it is seen that, when cobalt is used, the ratio of permanganate formed to that theoretically possible decreases in a regular manner as the amount of manganese salt used increases. In the case of copper, however, although the amount of permanganate formed approached the theoretical more closely than when cobalt was used, the results obtained were erratic. Occasionally, the manganese was completely converted into permanganate, and it was noticed that this happened only when the standard manganese solution (in this case prepared from permanganate) was slightly acidic. It was found impossible, however, to reproduce these conditions, as a very slight excess of acid over the alkali present in the hypochlorite caused decomposition to set in, whereas a deficiency of acid did not favour complete oxidation of manganese.

These indications that low alkalinity is a critical factor in the reaction find support on theoretical grounds. Kauffmann ("Bleichlaugen und Bleichverlauf," *Z. angew. Chem.*, 1924, **37**, 364) states that the activity of sodium hypochlorite is due to free hypochlorous acid, and that the condition of higher instability occasioned by a minimal alkali content is also that of enhanced activity. Again, assuming that it is peroxide of copper that catalyses the reaction

(and later observations seem to warrant this assumption), an appreciable hydroxyl-ion concentration would hasten its decomposition.

In view of the difficulty experienced in establishing and maintaining approximate neutrality during the course of the reaction by means of mineral acid, use was made of the solution of the double carbonate of sodium and copper (Aldridge and Applebey, J., 1922, **121**, 238), which has a very slight alkalinity. Owing to the buffer action of this solution, the addition of the alkaline hypochlorite does not appreciably alter the p_H value of the solution.

2 C.c. of a solution containing 100 g. of anhydrous sodium carbonate and 40 g. of sodium bicarbonate per litre were warmed to 50°, and 3 c.c. of copper sulphate solution (containing 1 g. of CuO per litre) were added. Into this solution was poured quickly a measured quantity of manganese salt solution, the liquid shaken, and, before any signs of turbidity appeared, 5 c.c. of 5*N*-sodium hypochlorite were added from a burette, whilst the flask was shaken. The liquid was diluted to 50 c.c., gently heated until freely effervescing, and then boiled for 3 minutes. Filtration through an asbestos–glass wool filter was followed by the addition of 1 c.c. of hypochlorite and 0·5 c.c. of saturated sodium bicarbonate solution. The solution was then cooled, made up to a known bulk, and the permanganate estimated colorimetrically.

	I.	II.	III.	IV.	V.	VI.	VII.
Manganese salt present	1·02	2·04	3·07	4·00	4·00	4·00	5·11
Permanganate formed	1·08	2·09	3·17	4·01	3·93	4·02	5·16

If the hypochlorite is not added immediately after the manganese salt has dissolved in the double sodium copper carbonate solution, the solution becomes turbid, and the amount of permanganate subsequently formed is decreased, as shown by the following figures (VIII—XII).

	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Manganese salt taken	2·04	2·04	3·06	3·07	3·07	4·00	4·00
Permanganate formed	1·86	1·73	2·80	2·85	2·81	3·79	3·89

A somewhat lower result for permanganate was also obtained if only 1 minute's boiling (instead of the usual 3 minutes) was given after reaching the stage of free effervescence (Nos. XIII and XIV).

When the modified procedure described above was applied to cobalt, considerably less permanganate was formed and appreciable quantities of cobalt remained in solution, rendering colorimetric estimation difficult, owing to the difference in tint between the standard and the sample.

The filtrates I—VII were tested for copper. They were evapor-

ated to dryness and the residues were dissolved in dilute acid, any copper present being separated as sulphide and estimated colorimetrically as copper pyridine thiocyanate (Spacu, *Bul. Soc. Stiinte Cluj*, 1922, **1**, 284). Only traces of copper were found, and these did not affect the tint of the permanganate.

			IV.	V.	VI.	
Mn salt taken	Nil.	Nil.	4·00	4·00	4·00	13·32
Cu salt taken (as mg. CuO)...	3·12	3·12	3·12	3·12	3·12	1·04
Cu salt in filtrate (as mg. CuO)	0·03	0·01	0·08	0·08	0·06	0·03

When sodium hypochlorite is added to the double copper carbonate solution alone, the solution acquires a deep yellow colour, and gradually deposits a buff precipitate, which, on heating, is converted into a dense black precipitate. This behaviour emphasises another advantage of the use of the double copper carbonate in the reaction under study, *viz.*, the introduction of the copper into the reaction mixture in a form which is soluble and not readily precipitable. It was found that, if the copper had once become separated as a brown flocculent precipitate (*e.g.*, by the method described on p.1471, and in the presence of considerable alkali), the dense black precipitate phase did not occur, and the amount of permanganate formed was far from theoretical, nor could it be appreciably increased by further treatment of the residue. This is in agreement with the work of Müller (*Z. anorg. Chem.*, 1907, **54**, 417) on the formation of copper peroxide by the action of hypochlorite on copper oxide, who found that he could obtain the yellow peroxide only by the use of a clear blue alkaline *solution* of copper oxide. When a *suspension* of cupric hydroxide in alkali was used, he could not observe the formation of either the yellow copper peroxide or the black copper oxide phase.

When the method described above was applied to larger amounts of manganese (above 8 mg. MnO), the quantity of permanganate formed did not reach the theoretical value (XV—XIX).

	XV.	XVI.	XVII.	XVIII.	XIX.
Manganese taken	13·33	13·07	13·33	13·33	13·33
Permanganate formed	12·00	12·23	11·82	12·23	11·68

It was thought that this might be due to the premature decomposition of the buffer solution by loss of carbon dioxide before the comparatively large quantity of manganese had been converted to permanganate. To retard this loss as far as possible, the experiments were repeated, a stream of carbon dioxide being passed through the solution during the heating. At the end of 3 minutes' heating, and without check in the passage of the gas, a further 10 c.c. of sodium hypochlorite were added from a burette. After

a further 2 minutes' heating the solution was filtered, and the permanganate estimated as before (XX—XXIII).

	XX.	XXI.	XXII.	XXIII.
Manganese taken	9·84	9·84	13·33	13·33
Permanganate formed	9·62	9·84	13·22	13·30

By this modified method practically all the manganese was converted to permanganate, as in the case in which smaller quantities of manganese were taken. Owing to the difficulty of estimating colorimetrically permanganate corresponding to more than 15 mg. of MnO, the method was not applied to amounts greater than this.

Reversibility of the Reaction.—When known amounts of permanganate were heated with approximately equivalent quantities of copper as double carbonate and with hypochlorite, no decrease in the amount of permanganate could be detected colorimetrically, and the precipitates, when tested by the bismuthate process, indicated only traces of manganese. It appears, then, that the reverse reaction is negligible in the case of copper, although when cobalt is substituted for copper an appreciable amount of permanganate is reduced.

Ratio of Manganese to Copper.—The most effective ratio of copper to manganese is not so well defined as is the case with other factors, and varies considerably according to the circumstances. For moderate amounts of manganese (1—5 mg. MnO), the presence of the equivalent quantity of copper leads to the best results, but with larger amounts of manganese the presence of approximately equivalent quantities of copper is not favourable to complete precipitation of the copper. Again, a large surface area of catalyst results in a relatively rapid decomposition of hypochlorite without perceptibly hastening the permanganate formation. This would have the effect of rendering the curve (Fig. 1) less steep, and delaying the attainment of the maximum value. With moderate amounts of manganese and very small quantities of copper, permanganate formation is incomplete, *e.g.*, 4·22 mg. MnO and 0·10 mg. CuO yielded permanganate equivalent to 3·70 mg. MnO. The precipitate was separated, washed, and heated with more hypochlorite, yielding a further 0·36 mg., and a third treatment of the precipitate gave 0·05 mg.

Increase in the ratio of cobalt to manganese shows a marked tendency to decrease the amount of permanganate formed.

Limit of Delicacy for Detection of Manganese.—The minimal quantity of manganese that could be detected by this method appeared to depend on the amount of permanganate capable of producing a visible tint: Manganese equivalent to 0·002 mg. MnO

was converted to the theoretical amount of permanganate. For this purpose only 0·5 c.c. of sodium hypochlorite and 0·2 c.c. of sodium copper carbonate solution were used; a larger quantity of hypochlorite tended to mask the permanganate colour with a yellowish tint.

Mechanism of the Reaction.—It is evident that there is a pronounced difference between the functions of the copper oxide and of the cobalt oxide in this reaction:

(1) The hydroxyl-ion concentration, which is so critical a factor in the case of copper, appears to be comparatively unimportant in the case of cobalt, although large concentrations of alkali are prejudicial to permanganate formation.

(2) Other conditions being favourable, moderate amounts of manganese salts can be completely oxidised to permanganate in the presence of copper, independent of the amount of manganese present. When cobalt is used, however, the proportion of permanganate formed decreases in a regular manner with increasing amounts of manganese.

(3) The form and the mode of action of the precipitates of cobalt and copper differ in several respects. That of cobalt is flocculent, finely divided, and difficult to filter, and promotes copious evolution of oxygen from the hypochlorite throughout the reaction. The copper precipitate, at first flocculent, soon passes into a dense black residue, easily separated, and becomes considerably less active as regards hypochlorite decomposition after the formation of the permanganate has taken place.

(4) The cobalt, when used in the form of the double sodium carbonate, cannot be completely separated from the solution by boiling, as is the case with moderate quantities of copper.

It is suggested that the following probably represents the course of the main reaction, and is in agreement with the facts described in the foregoing pages. The first effect of the hypochlorite is to form copper peroxide and hydrated manganese dioxide. The oxidation of manganese dioxide to permanganate, which can proceed in the presence of manganese alone, is greatly accelerated by the copper peroxide, which gives up its active oxygen, possibly through the intermediate formation of an unstable compound of copper and manganese,* and is reconverted to the cupric form. At this stage

* Some evidence for the existence of such an unstable intermediate compound is afforded by the following observations. If the manganese and copper salts are separately warmed with hypochlorite before mixing, and the combined solutions heated with a further quantity of hypochlorite, the amount of permanganate formed is much less than that obtained by the action of hypochlorite on the mixed salts.

much of the hypochlorite has been decomposed, and the hydroxyl-ion concentration, due to the alkali which is necessarily present in the hypochlorite solution, becomes an important factor. The excess of hydroxyl ions has an inhibitive effect on the formation of fresh copper peroxide, and the main reaction is arrested. If, however, the carbonate–bicarbonate mixture is used, (i) its buffer action renders the influence of the alkali negligible, and (ii) owing to the delayed precipitation of the copper, much of the earlier part of the reaction takes place in the liquid phase, and the oxidation of the manganese proceeds to completion.

BATTERSEA POLYTECHNIC. [*Received, March 28th*, 1927.]

CXCIX.—*The Activation of Wood Charcoal by Progressive Oxidation in Relation to Bulk Density and Iodine Adsorption.*

By ALBERT BRAMAH PEARCE PAGE.

PROGRESSIVE oxidation of wood charcoal alters its sorptive capacity, but a systematic study of this alteration requires a stock material, the properties of which do not vary much from one charge to the next. To make a standard charcoal from a pure chemical compound, it may be sufficient to fix the conditions of carbonisation, but this is not true for wood charcoal, on account of the heterogeneity of wood. Accordingly, in the present work, the conditions of carbonisation were fixed only approximately, exact similarity of every quantity of charcoal taken for subsequent treatment being ensured in the following way.

The wood was carbonised in the form of cubes, which were so small that there were a very large number in a furnace charge. Since these cubes were roughly mixed and the conditions of carbonisation fixed approximately, it is likely that the charcoal from the different charges was fairly uniform. Each of these charges of charcoal was then most thoroughly mixed with all the other charges according to a definite plan, thus rendering it extremely probable that any one portion taken for subsequent treatment was a representative sample.

The standard charcoal was oxidised at various temperatures by a slow stream of air or of an oxygen–nitrogen mixture rich in nitrogen. This mode of oxidation was chosen because (*a*) it was a natural development from earlier rough experiments with crucibles more or less open to air; (*b*) it was readily controlled by varying the proportion of oxygen in the gas stream, and it allowed all the

important variables to be fixed; and (*c*) it seemed likely to lead to the most simple series of reactions.

The labour and time involved necessitated the examination of the treated charcoals by simple methods. Those chosen as being the most informative were the "bulk density" test and the determination of the removal of iodine from solution in benzene. These two simple tests were applied to a very large number of charcoals, all made from the standard stock.

Experimental.

Preparation of Stock Charcoal.—Birch wood, cut into rough ½-inch cubes, was carbonised in a horizontal silica tube closed with asbestos wool. The tube was kept in a well-lagged electric furnace for 4 hours, after which it was withdrawn, allowed to cool for about ½ hour, and then unloaded. The furnace kept the interior of the tube at 400° in the absence of any charge. The charcoals obtained from 64 charges—each of which was bottled separately—were thoroughly mixed according to a plan which will be apparent from the following description for the first 8 charges. Each of the original charges 1, 2, 3, . . . 8 was divided into 8 equal parts a, b, c, . . . h. Parts 1a and 2a were mixed, giving 1.2(a). Similarly the mixed parts 1.2(b), etc., and 3.4(a), 3.4(b), up to 7.8(a), (b) . . . (h) were obtained. Then the parts 1.2(a) and 1.2(b) were themselves mixed, giving 1.2(a.b), the corresponding parts from the other charges being similarly treated. Repetition of this process gave the four mixed charges 1.2(a.b.c . . .h), 3.4(a.b.c . . . h), 5.6(a.b.c . . . h), and 7.8(a.b.c . . . h), which were now called (1.2), (3.4), (5.6), and (7.8). Each of these was divided into 16 equal parts, which were then mixed as before to give, after several mixings, the two mixed charges (1.2.3.4) and (5.6.7.8). Each was divided into 32 equal parts, which were then mixed in the same manner to give eventually the mixed charge (1.2.3.4.5.6.7.8). The mixed charge (1.2.3 . . . 64), when sieved free from dust, was the stock charcoal, the oxidation of which has been studied.

Conditions of Heat Treatment.—(i) *Temperature.* The temperature of the charcoal during heat treatment was taken as that given by a platinum–rhodium couple the junction of which was immediately over the pile of charcoal. Occasional regulation of a long and well-lagged wire resistance furnace prevented fluctuations of more than 5° from the required value.

(ii) *Atmosphere.* Mixtures of oxygen and nitrogen at atmospheric pressure were passed at known rates over the charcoal. The oxygen contents (by vol.) of mixtures 1, 2, 3, and 4 were,

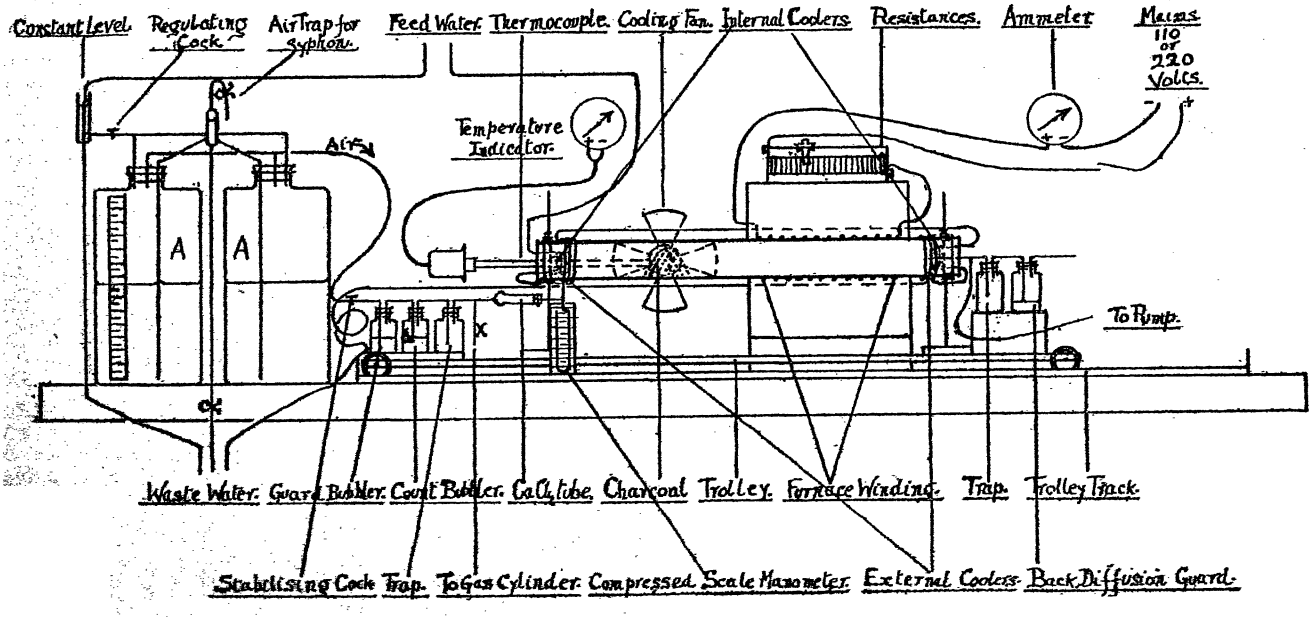
respectively, 21, 10, 2, and 0·5%, the first being air, and the other three being supplied in cylinders by the British Oxygen Co., Ltd. —these were analysed in a Bone–Wheeler apparatus. In a short experiment, the effect of the oxygen in the 0·5% mixture appeared to be negligible. There was no reason, therefore, to use pure nitrogen.

The rate indicator was a sulphuric acid bubbler with a jet ground off square. It was protected on both sides, and the complete train was calibrated, yielding a curve showing the rate of delivery of gas in litres per hour corresponding to the number of bubbles per minute. The bubbler was quite suitable for the slow rate of 0·7 litre per hour which was nearly always used. Regulation of the rate of mixtures 2, 3, and 4 was obtained by the main needle valve. This required altering every 2—4 hours. Mixture 1 (air) was taken under a pressure of a few inches of water from the two 15-litre bottles A,A (Fig. 1). Rate regulation was effected by the cock shown, whilst the "stabilising cock" served as a steadying resistance to ensure even bubbling. The actual volume of air used was read from a scale on one of the bottles, which showed the combined contents of the bottles for various water levels.

(iii) *Time of treatment.* To define the time of treatment, the charcoal must be both heated and cooled quickly. The long horizontal containing tube (Fig. 1) was carried on platforms which formed a trolley running beyond the furnace at either end. To perform an experiment, the trolley was pushed to the left (as in the figure) and the cooling fan switched on. The weighed charge (27 g.) was loaded into the tube and pushed into a conical heap in the position shown. The tube was closed with water-cooled bungs, lubricated with glycerol, one carrying the thermo-couple, and the other the exit tube, which led to the trap and guard bubbler, and to the pump. The gas entered by a T-piece connected also to a closed manometer which was used in the preliminary displacement of air by three alternate evacuations and fillings with gas. The bubbling rate was adjusted and the cooling fan switched off. The voltage across the furnace was raised from its normal value to that of the main, *viz.*, 220 volts. The trolley was pushed to the right, so as to bring the charcoal into the middle of the furnace. The annular space between the containing tube and the furnace was closed at both ends with asbestos wool. In about 15 minutes the current was altered to that needed to maintain the desired temperature. The treatment was considered to have begun when the temperature had risen to within 10° of that required, and to have ended at the moment the trolley was run back to the left and the cooling fan switched on. Within 5 or 10 minutes, the

Diagram of Heat Treatment Apparatus

Fig. 1.



temperature indicated had fallen to 400°. At this temperature, activation is very slow. At 50° the treated charcoal was raked into a tared beaker and weighed.

(iv) *Other variables.* Variable conditions, such as size and shape of charcoal particles and disposition of apparatus, affecting the circulation of gas among the particles, were maintained roughly constant. Doubtless such irregular results as were obtained were partly due to these variations, which would be most marked when but little charcoal remained unburnt.

Examination of the Treated Charcoals.—After the selection of 12 representative cubes, the remainder were broken up to give a maximum yield of particles between 10 and 20 to the inch. Each block was cut into $\frac{1}{10}''$ sections, across the grain. The charcoal retained by the "10" sieve after this treatment was placed a little at a time in a flat mortar and tapped lightly. Most of it lay on its end grain and so split into small cubes instead of the usual thin strands or powder. The charcoal which passed the "20" sieve was ground in a glass mortar to yield equal quantities of "100—200" and "less than 200" charcoal. The "10—20" size, intended for gas adsorption, has not yet been used. The "100—200" size proved convenient for "bulk-density" tests. The "less than 200" size was used for sorption from solution.

Determination of bulk density. About 6 c.c. of the "100—200" charcoal spread over the bottom of a flat weighing-bottle remained over calcium chloride in a vacuum desiccator for about 12 hours. It was then weighed and transferred from glazed paper by a brush to a narrow test-tube of 7 c.c. capacity, graduated in tenths of a c.c. This tube was held vertically at one end of a horizontal arm which was pivoted at the other end, $21\frac{1}{4}''$ away. The arm carried a pin, bearing on a cam driven at 100 r.p.m. by a shunt motor, and so shaped that the arm and tube were gently raised and then given a clear drop of 1″ at every revolution. After 15 minutes, *i.e.*, 1500 "taps," the tube was removed and the "bulk volume" of the charcoal read to 0·02 c.c. after carefully levelling the surface by striking the tube gently at the side with the finger. The tube, replaced in the "tapper," was given a further 500 taps, and the volume read again. Agreement worse than 0·01 or 0·02 c.c. indicated incomplete drying or sieving, and hence the need for a complete redetermination. The weight of the charcoal (in mg.) divided by the bulk volume (in c.c.) gives the bulk density.

Determination of activity or sorptive capacity. The iodine used was purified in the usual way and tested by titration against sodium thiosulphate solutions standardised against pure recrystallised potassium dichromate. The benzene was purified according to

Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825; 1919, **41**, 2002). The solutions of iodine in benzene were estimated by direct titration with sodium thiosulphate in presence of aqueous potassium iodide. As seen by a "daylight" lamp, the disappearance of the pink colour from the benzene layer was quite sharp even with *N*/100-solutions. Fifty or 100 determinations were made at a time by the following method. Soft-glass test-tubes were cleaned, dried, numbered, and weighed, and about 0·25 g. of charcoal was weighed roughly into each. After drying in a vacuum desiccator, the tubes were quickly stoppered with compressed cotton wool, which was not removed until a rider adjustment sufficed to complete the weighing. The weighed tubes were placed in a numbered rack and each was drawn out. After solution had been added in the proportion of 100 c.c. per g. of charcoal, the tubes were sealed with a hand blow-pipe. After being shaken for a definite period, each tube was tapped so as to remove charcoal and solution from the tip and then put in its place in a numbered rack. Soon the suspended charcoal settled, the tip was cracked off, and the clear solution decanted and titrated.

Nomenclature. All the treated charcoals are numbered as follows. First, a number expressing the temperature at which the charcoal was treated, *e.g.*, 500, 600 . . . 900; secondly, separated from it by a stroke (/), a number, of four digits, expressing in litres the total volume of oxygen, at atmospheric pressure and room temperature, passed over the charcoal at the standard rate of 0·7 litre per hour, *e.g.*, /00·01 or /12·30. Thus, a charcoal treated at 0·7 litre per hour for 10 hours at 600° with gas containing 2% of oxygen would be labelled 600/00·14. If a rate other than 0·7 litre per hour were used, a special note is added, *e.g.*, 500/02·38 (14 l./hr.).

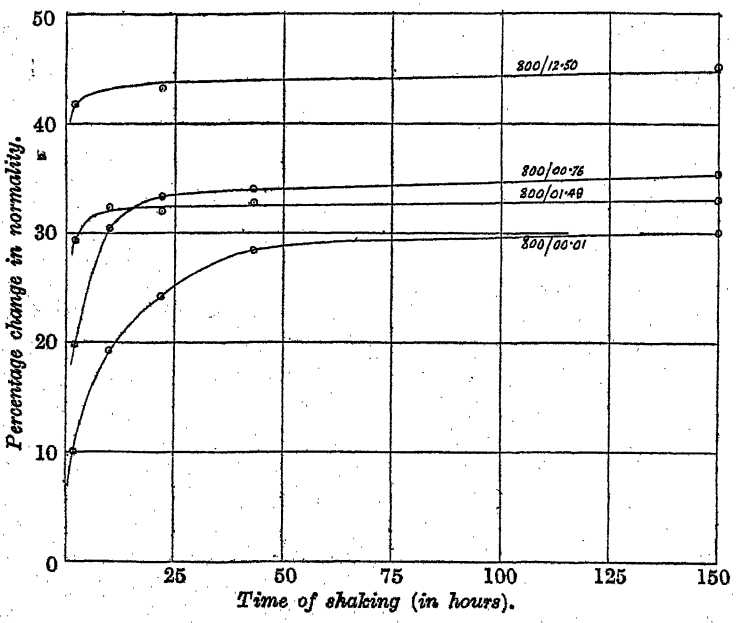
Properties of the Treated Charcoals.—(1) *Appearance.* Every block appeared shrunken. The following general statements may be made: (*a*) For 2 or 3 litres of oxygen or less, the charcoal was harder and, although still definitely black, had acquired a slight lustre. This was most pronounced at high temperatures. (*b*) For 4 or 5 litres of oxygen or more, the charcoal seemed softer. (*c*) At 500° and 600°, the charcoal burnt away much as sticks in a bonfire with a large, loose, white ash. When separated from this, and cut or powdered, the charcoal was sooty black. The three heavily oxidised charcoals treated at 600°, 600/10·29, 600/14·33, and 600/20·58, were very soft and broke up to an intensely black soot. (*d*) At 800° and 900°, the charcoal burnt away without much separation of loose ash. The cubes compacted and decreased in size until there remained a tiny grey cube; this was very fragile, but

was sometimes removable from the tube, and must have been nearly all ash. The heavily oxidised charcoals were soft but not sooty. Those treated at 900° were noticeably flaky. (*e*) The 700° charcoals seemed intermediate between those mentioned in (*c*) and (*d*).

(2) *Rate of sorption of iodine from benzene solution, and the ageing effect.* In all the experiments with freshly treated charcoal the duration of shaking was 22 hours. According to Davis (J., 1907, **91**, 1663), McBain (*Trans. Faraday Soc.*, 1919, **14**, 202), and others,

FIG. 2.

Rate of sorption of iodine from N/10-*solution in benzene by four different charcoals.*



adsorption should be complete in a shorter time, and absorption not noticeable until after a much longer time. Some peculiar isotherms for charcoals prepared at 600°, 700°, and 800° with little oxygen threw doubt on this. Accordingly, it was decided to determine the rate of sorption from *N*/10-solution by the four typical charcoals 800/12·50, 800/01·49, 800/00·76, and 800/00·01. The results are plotted in Fig. 2.

The distinction between *ad*- and *ab*-sorption is not clear. Although the order of figures is the same at 22 as at 150 hours' shaking, yet the absolute values are very different. In particular, the figure for charcoal 800/00 01 at 22 hours is 6% low. Evidently the /00·01

charcoals are exceptional. The contention of Herbst that a slow rate of sorption is due to a high density is not upheld. Other factors must be more important, for the bulk densities of 800/00·01, /00·76, and /01·49 are about the same. McBain's "cleaning" of the surface is possibly one such factor. There is an undoubted ageing effect which may account in part for the slow rate of sorption. It will be seen from the general tables that the sorption from $N/5$- and $N/10$-solution, after shaking for 150 hours with charcoals which have aged, is less than that brought about by shaking for 22 hours with freshly treated charcoals. But this ageing effect cannot account entirely for the slow rate, for the sorption from $N/20$-solutions is about the same, whilst from $N/50$-solutions it is greater when brought about by shaking for 150 hours with aged charcoals than for 22 hours with fresh charcoals. This would probably be even more marked at higher dilution. The ageing effect is irregular, for although the individual isotherms for aged charcoals with long shaking are smoother than the others, yet the isotherms for a series of charcoals are related for the short period and unrelated for the long period. There is no evidence indicating the cause or nature of the effect. It may possibly correspond, in part, to the formation of a stable carbon–oxygen complex from the catalytic carbon surface and adsorbed oxygen (see Rideal and Wright, J., 1925, **127**, 1347).

(3) *Influence of the rate of passage of gas.* This can be deduced from the general tables (for eight charcoals), but is of little interest. It is noteworthy, however, that, for a given percentage yield, the charcoals prepared with a fast gas stream are less active than those with a slow stream. It is possible that at the fast rate either some of the active carbon may be removed mechanically, or, since there may be more oxygen available at any instant, more of the active carbon formed (or freed) is burnt away or perhaps covered with a "Langmuir film" of firmly attached oxygen.

(4) *Significance of the total amount of oxygen.* It was soon found that the properties of charcoals treated at any one temperature with a gas stream of 0·7 litre per hour depended almost solely on the *total* amount of oxygen passed, and if this was kept constant, they varied comparatively slightly with the joint alteration of time of treatment and oxygen concentration. This is shown in Table I.

TABLE I.

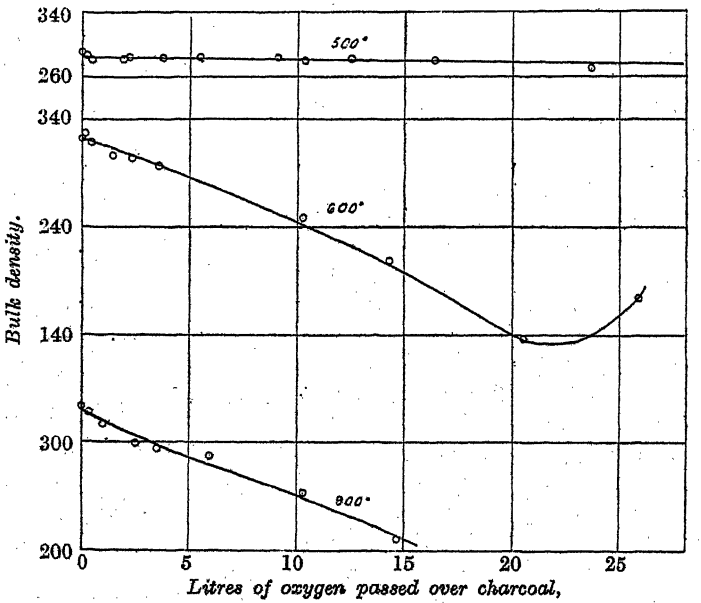
	Activity towards $N/10$-solutions.	
Name of charcoal.	Charcoal treated 4 hours in 2% O_2.	Charcoal treated 16 hours in 0·5% O_2.
400/00·06	7·4	8·0
600/00·06	39·9	40·0
900/00·06	4·9	5·6

the change in activity when the total oxygen is constant being within the limits of experimental error. At the same time, during long experiments there was probably some distillation, and the effect of the change of oxygen concentration from 21% in Mixture 1 to 0·5% in Mixture 4 cannot have been entirely negligible.

(5) *Effect of temperature change and variation in the total amount of oxygen.* The yield of charcoal treated at any one temperature falls off directly with increase in the total volume of oxygen passed. There is a tendency for it to fall less quickly when but little char-

FIG. 3.

Variation of bulk density with degree of oxidation of charcoal.



coal remains unburnt, and less quickly at low than at high temperatures. These changes can be seen by plotting the data given in the main tables.

The Bulk-density Curves.—In Fig. 3 is shown the variation of bulk density with oxidation at 500°, 600°, and 900°. It will be seen that the bulk density of charcoals treated at 500° is nearly constant and independent of the amount of oxygen used. That of charcoals treated at 600° and 900° falls off regularly with oxidation. With excessive oxidation the bulk density of the charcoals treated at 600° eventually rises after passing through a minimum. This rise is probably due to a very high ash content, most of the carbon having been burnt away. Associated with it is a low

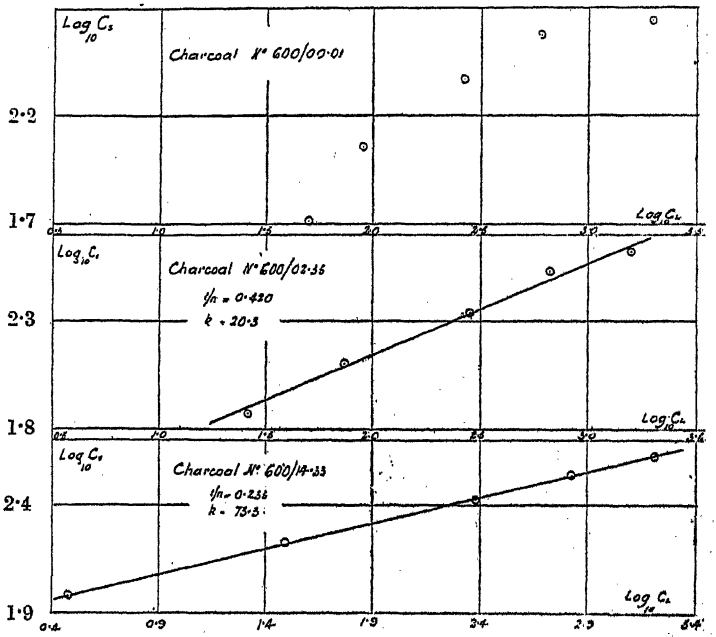
activity towards $N/10$-iodine solution. The irregular fluctuations of the bulk density of slightly oxidised charcoals are probably fortuitous. The curve for charcoals treated at 700° is similar to the 600° curve. The 800° curve flattens at the highest degree of oxidation used and would probably rise with further oxidation.

Sorption of Iodine from Benzene Solution.

(i) *The "Freundlich" Constants.*—To characterise the activity of each treated charcoal, adsorption isotherms have been obtained

FIG. 4.

Typical logarithmic adsorption isotherms for charcoals treated at 600°.



with iodine in benzene solution. The concentrations used were $N/5$, $N/10$, $N/20$, $N/50$, and $N/100$ with 22 hours' shaking, and $N/5$, $N/10$, $N/20$, and $N/50$ with 150 hours' shaking. The concentration in the solid phase, C_S, is expressed in terms of c.c. of $N/100$-solution containing the iodine adsorbed per g. of charcoal; and that in the liquid phase, C_L, is similarly expressed per 100 c.c. of solution. No account has been taken of the removal of the benzene by the charcoal. Curves were drawn showing the change of $\log_{10} C_S$ with $\log_{10} C_L$ for each charcoal. Most of these curves are fair straight lines, and from them have been calculated the constants in the Freundlich equation ($C_S = kC_L^{1/n}$), k being the

concentration in the solid phase when that in the liquid is equal to unity, and $1/n$ the slope of the line. The three curves in Fig. 4 are representative of those obtained from experiments with 22 hours' shaking. With 150 hours' shaking, there was, on the whole, considerably closer approximation to the straight line. The curve for charcoal 600/00·01 is an extreme example of the curvilinear form obtained with very slightly oxidised charcoals treated at temperatures below 850°. Most of the charcoals treated at 500° give similar curves. The other two curves are fair samples of the bulk; that of charcoal 600/02·35 is the first of the 600° curves from which constants have been calculated.

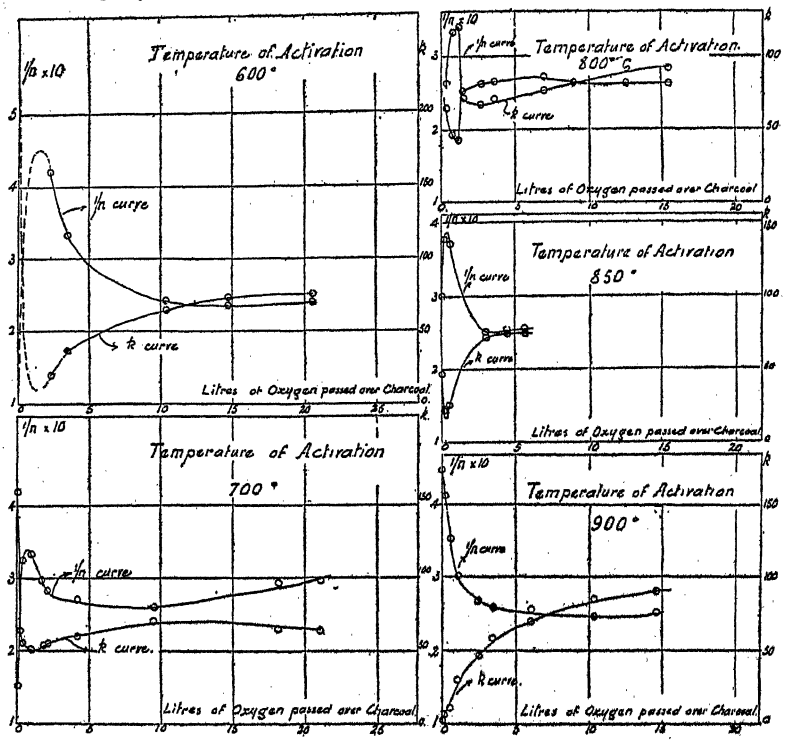
The interpretation of the changes in these constants (k and $1/n$) depends, in the first place, on the following considerations. For any one isotherm, $1/n$ is a characteristic constant and depends only on the ratio of the units chosen for C_S and for C_L. Its variation, from one isotherm to another, is not even dependent on the particular value of this ratio, provided this is kept constant. On the other hand, k depends on the magnitude of the units chosen. Further, since two isotherms will cross each other at concentrations higher or lower than C_L = one unit, according to the magnitude of the unit, therefore the *relative* value of k for the two isotherms will also change. Now C_L is expressed in very small units, so that it happens that the crossing point of most of the isotherms is at liquid concentrations higher than $C_L = 1$. (This can be seen by plotting, and follows also from the reciprocal variation of the constants from one isotherm to another, which is most marked—see curves in Fig. 5.) Hence a change in the value of k, accompanied as it is by a reciprocal change in the value of $1/n$, actually indicates a change in sorption at low concentrations, whilst the magnitude of $1/n$ indicates the extent to which the sorption falls off at higher concentrations compared with simple proportionality.

(ii) *Variation of the Constants with Temperature and Total Amount of Oxygen.*—For 22 hours' shaking, the variation of k and $1/n$ with the volume of oxygen passed over the charcoal at 600°, 700°, 800°, 850°, and 900° is shown by the curves in Fig. 5. The scales of plotting are, of course, arbitrary; therefore, the maxima and minima and the points of inflexion are the only characteristic features. The curves for 600° are traced no nearer to the zero oxygen axis than 2·35 litres of oxygen, because the shape of the isotherms of the less oxidised charcoals did not permit the evaluation of the constants. The values for the slightly oxidised charcoals at 700° and 800° are from lines on the logarithmic graphs drawn through points derived from measurements with $N/5$-, $N/10$-, and $N/20$-solutions, the experiments in which the shaking was pro-

longed to 150 hours having shown that the systems with the more dilute solutions were probably far short of equilibrium. Very few of the 500° charcoals give isotherms from which constants can be calculated even after the long period of shaking. This slowness in attaining equilibrium was one of the important points brought out by the experiments with long shaking. The other was the clear demonstration of the ageing effect. Unfortunately, as previously

FIG. 5.

Change of Freundlich constants with degree of oxidation of charcoal.



mentioned, the irregularity of this effect has concealed the relations of the constants obtained from these experiments with 150 hours' shaking.

The reciprocity of the k and $1/n$ curves shows, as already stated, that, in general, the isotherms cross one another at concentrations higher than $C_L = 1$, *i.e.*, higher than $C_L = 0{\cdot}0001N$. On comparing all the isotherms, many crossing points will be found between $C_L = 0{\cdot}0002N$ and $0{\cdot}193N$, *i.e.*, within the range which includes $N/10$-, $N/20$-, and $N/50$-solutions, one of which is frequently used

for determining activity (compare Ruff, *Z. angew. Chem.*, 1925, **38**, 1164; Berl and Wachendorff, *Koll. Z.*, Special No., April, 1925, pp. 36—40). From this it follows that determinations of activity made at only one concentration are, in general, misleading.

The curves obtained by plotting k and $1/n$ as ordinates against volumes of oxygen as abscissæ are steepest near the zero oxygen axis. There is a family resemblance between the curves at the five temperatures. On the zero oxygen axis, the highest value of k is probably at 600°, as indicated by the dotted line suggested for the shape of the 600° curve over the range where no figures are obtainable. From 600° the initial value of k decreases continuously with temperature to a very low value at 900°. The subsequent fall of k with increasing value of oxygen also varies with temperature in the same sense from 600° to 850° inclusive. At 850°, the fall is small, whilst at 900° it is non-existent; k, at that temperature, increases continuously with the volume of oxygen from its very low initial value to about the same as that attained by the 800° curve. This continuous increase in k, which forms the whole curve at 900°, corresponds to the only clearly marked feature of the curves at the other temperatures after the initial fall in the k values has been passed. The curves at 700° and 800° certainly have a more complicated form, but it cannot be decided whether this is due chiefly to experimental error or not. It is rather remarkable that these derived curves, expressing the properties of so variable a substance as charcoal, should show resemblances as clearly as they do. The $1/n$ curves exhibit somewhat similar resemblances.

The extent of the variation of $1/n$ is surprising when it is recalled that the charcoals which show it have all been prepared from the same stock charcoal; for the magnitude of $1/n$ expresses, as already stated, the extent to which sorption falls away at high concentrations from simple proportionality, and must indicate a change in type or disposition of surface rather than the mere enlargement which might be expected to result from progressive oxidation.

Strictly, since k and $1/n$ are characteristic of the whole system and not of the charcoal alone, it is difficult to interpret their changes in terms of changes in the charcoal. (It may be recalled that Firth, *Trans. Faraday Soc.*, 1921, **16**, 434, found that the constants for the system iodine–*benzene*–charcoal differed from those for the system iodine–*chloroform*–charcoal.) Besides this difficulty, there is the solvent correction, which is uncertain, although of little importance at the low concentrations used. If, however, the constants k and $1/n$ are conceded to be relatively characteristic of the charcoal, then the following suggestions may be put forward to account for their variation.

Theory of the Variation of the Freundlich Constants.—The changes from one charcoal to another, which may be responsible for the observed variation of k and $1/n$, will first be considered. Since the solution wets the charcoal there must be a definite attraction between the two. Further, the equilibrium concentration of iodine in the bulk of the solution is less than that at the solution–charcoal interface; hence, there is a decrease of surface energy accompanying adsorption, and more energy is liberated in the adsorption of iodine by the charcoal than in the adsorption of benzene. This will hold whatever be the mechanism of the adsorption, whether the attracting field of force above the charcoal surface is uniformly distributed over the surface or localised at active spots, whether it extends for only one molecular diameter or for many, or whether it varies so that in effect only every x atoms of carbon can attract one adsorbed molecule. An increase of available surface per gram of charcoal would merely increase the value of k.

A change in the value of $1/n$ would entail either (i) a change in the field of force, involving the creation of, or an alteration in, an interference effect between the adsorbed molecules; or (ii) a change in the relative importance of two or more types of attraction.

It is easy to see that (i) might be brought about either by a molecular rearrangement of the surface producing a change in the closeness of packing of the adsorbed molecules or by a change in the disposition of the available surface producing locally, according to the size and shape of the capillaries, a change in the closeness of packing.

Since adsorption depends on the specific attraction of the carbon in charcoal, it follows that if there is more than one type of carbon, as Chaney assumed (*i.e.* presumably, more than one type of crystal lattice), then a change in the proportions of these types would bring about change (ii) above.

Rideal and Wright (*loc. cit.*) distinguish three types of surface, and it may be that investigation of the charcoals on the lines of their method would have furnished a satisfactory characterisation. The attempt, however, has been made to interpret the results obtained in the present investigation on the basis of change (i) above.

A brief summary of the variations of k and $1/n$ is of use in considering the corresponding variations in the charcoal: (i) $1/n$ varies from one charcoal to another; (ii) k and $1/n$ vary reciprocally, as a rule; (iii) k and $1/n$ always vary simultaneously; (iv) the k and $1/n$ curves for 600°, 700°, 800°, and 850° charcoals can most readily be built up from simple curves of two quantities, one of which decreases, whilst the other increases with oxidation. Now

bulk density decreases with oxidation, except that with excessive oxidation it has been shown for charcoals prepared at 600° and 700° to increase again after passing through a minimum. Philip, Dunnill, and Workman (*loc. cit.*), and others, have correlated bulk density with activity, and have suggested that with decrease of bulk density there is an *increase of available surface* which accounts for the observed increase in activity. This view seems reasonable, and is further supported by the present work if we exclude for the moment those charcoals prepared with very little oxygen, *i.e.*, less than 1 or 2 litres, at temperatures below 900°. In particular, the view is supported by the decreasing sorption (from $N/10$-solution *) which accompanies increasing bulk density of the most highly oxidised charcoals prepared at 600° and 700°. If this view is accepted, then both the increase of k and the decrease of $1/n$ receive a reasonable explanation. We have only to picture, along with the increase of the extent of surface, a change in the disposition which would increase the packing effect. This packing effect would obviously be more important at high than at low concentrations, so its increase would lead to a decrease of $1/n$. It is easy to see that if the oxidation increased the surface by rendering more and more capillaries available, then in these capillaries a packing effect would not be unlikely.

In seeking a quantity likely to *decrease* with oxidation, in order to suggest a change in the charcoal responsible for the changes in the first part of the k and $1/n$ curves, the rapidity of these changes must be borne in mind. The quantity must alter so as to bring about a large change at 600° and 700°, a smaller change at 800° and 850°, and none at all at 900°; further, its alteration must bring about these changes over a range of oxidation, over which other quantities, such as bulk density and yield, vary very little. It is suggested that this quantity must be the effective number of attracting centres per unit of surface. It may also be described as a particular configuration of the surface giving *in effect* a large number of active centres, and may correspond to what Chaney describes as a particular modification of carbon in an "active" state. We may readily imagine that this quantity would have quite different values, initially, at different temperatures, as is required, varying from a low value or zero at 900° to a maximum at 600°. It is not difficult to see that the effect of oxidation might well be to decrease this quantity rapidly, either by the removal of the active centres (or the "active carbon") or by the formation of a firm "Langmuir adsorption compound." Since the bulk

* There was not sufficient charcoal left after oxidation to determine the sorption from solutions of other concentrations.

density of the unoxidised charcoals is high, therefore the available surface is probably small, so that the large number of active centres involves a large number of these centres per unit area, and therefore favours a large packing effect, giving a low value of $1/n$ and a high value of k. The rapid decrease in the number of active centres with oxidation causes a corresponding decrease in k and increase in $1/n$.

Iodine in benzene solution: 22 hours' shaking.
Percentage change in normality at various concentrations.

Charcoal No.	Bulk density.	Yield, %.	$N/100$.	$N/50$.	$N/20$.	$N/10$.	$N/5$.
500/00·01	302	76·6	44·2	—	—	23·8	14·7
500/00·25	299	76·4	—	—	—	26·6	15·5
500/00·46	296	76·4	41·5	—	—	27·0	15·8
500/01·13	309	74·9	—	—	—	27·4	—
500/01·83	295	73·8	—	—	—	26·2	15·8
500/02·14	298	74·5	33·9	—	—	26·9	15·4
500/03·76	296	69·4	43·3	—	—	29·9	16·0
500/05·46	297	66·0	44·8	—	—	32·0	17·1
500/09·01	296	60·8	49·8	—	—	31·8	17·3
500/10·33	292	56·7	—	—	—	20·5	16·5
500/12·50	294	53·0	55·6	—	—	30·6	—
500/16·34	293	47·0	—	—	—	27·6	16·7
500/23·63	285	31·2	66·1	—	—	28·4	18·2
500/31·16	294	16·7	77·2	—	—	29·3	17·4
600/00·01	322	74·1	51·1	56·5	46·4	38·9	21·6
600/00·06	325	82·6	55·4	—	—	39·9	—
*600/00·06	322	73·9	—	—	—	40·0	21·8
600/00·22	326	71·9	—	63·2	—	41·2	23·4
600/00·28	321	73·9	58·9	61·2	48·8	41·0	—
600/00·42	316	73·9	—	—	—	41·2	—
600/00·59	310	71·9	67·5	72·5	—	41·3	—
600/01·40	306	68·9	73·6	74·1	55·4	40·2	22·5
600/02·35	302	68·5	74·0	63·2	43·3	34·2	20·5
600/03·53	296	66·0	85·4	69·8	47·0	32·5	20·0
600/10·29	248	61·4	94·8	79·5	48·0	32·5	18·7
600/14·33	208	40·4	96·95	84·4	52·2	33·9	20·4
600/20·58	138	24·8	96·6	84·0	54·3	36·6	21·2
600/25·87	174	15·9	—	—	53·7	33·0	—
†600/05·88	309	66·0	—	—	—	25·0	—
‡600/11·76	298	50·4	—	—	—	27·2	—
700/00·01	—	72·3	—	86·2	67·7	41·0	23·8
700/00·20	320	70·7	96·8	82·5	63·6	40·4	27·6
700/00·39	337	71·9	—	77·0	58·7	43·9	27·6
700/00·92	324	70·5	94·8	78·3	61·0	41·8	25·8
700/01·74	316	68·9	96·5	74·3	54·7	34·7	23·4
700/02·14	308	67·0	—	77·4	52·7	33·5	21·7
700/04·22	289	61·5	98·1	79·0	50·4	34·2	21·6
700/09·49	256	47·4	98·4	84·6	55·2	35·9	23·2
700/12·39	236	37·4	—	—	—	39·6	23·5
700/18·14	206	26·3	98·5	86·0	56·8	41·2	26·2
700/21·06	199	17·8	97·3	86·5	58·2	42·0	26·1
700/25·33	237	4·1	—	—	—	34·2	—

* 16 Hours. † 7 Litres per hour. ‡ 14 Litres per hour.

Charcoal No.	Bulk density.	Yield, %.	*N*/100.	*N*/50.	*N*/20.	*N*/10.	*N*/5.
800/00·01	333	68·9	59·0	58·7	43·9	31·7	18·2
800/00·11	315	67·8	—	—	—	33·6	—
800/00·21	313	66·7	95·4	—	—	33·7	21·1
800/00·35	310	63·4	95·6	82·2	52·4	35·4	21·4
800/00·76	331	67·0	84·9	76·5	54·2	41·0	23·2
800/01·13	325	65·2	—	74·8	52·0	38·4	22·8
800/01·49	318	63·0	96·6	84·2	52·7	34·0	20·5
800/02·77	293	58·2	97·6	87·6	56·6	33·8	22·3
800/03·57	286	53·8	97·7	88·4	59·2	39·0	24·7
800/06·91	256	39·6	—	90·2	63·2	42·2	26·6
800/08·84	240	32·2	97·6	90·0	61·4	43·0	25·9
800/12·50	216	17·4	97·6	90·8	66·4	45·8	—
800/15·48	210	10·7	97·8	90·7	66·5	46·1	30·0
850/00·01	330	72·2	—	—	47·3	26·6*	20·4
850/00·09	321	65·6	78·2	—	38·2	30·5	18·4
850/00·59	310	62·2	—	61·3	41·2	29·2	19·1
850/03·05	291	54·5	97·2	—	56·0	36·4	23·1
850/04·45	275	45·6	97·3	—	57·0	38·1	23·9
850/05·67	266	41·9	97·1	—	58·9	38·9	—
900/00·01	330	70·5	16·1	11·5	—	4·8	3·3
900/00·06	327	71·5	—	—	—	4·9	—
†900/00·06	328	71·1	—	—	9·9	5·6	—
900/00·22	326	68·2	26·3	22·6	17·7	9·6	7·0
900/00·28	334	70·0	—	—	—	10·0	—
900/00·59	319	68·5	45·1	36·7	18·9	12·2	—
900/01·03	316	66·0	72·3	58·4	35·1	22·7	12·9
900/02·35	296	60·0	88·0	71·1	41·6	28·2	16·3
900/03·52	292	53·8	93·0	79·0	49·0	32·5	19·8
900/05·88	279	41·2	93·9	—	56·7	37·8	26·5
900/10·29	254	29·6	97·9	90·8	62·7	41·2	25·2
900/14·70	210	14·1	98·0	93·6	68·6	43·2	29·1
‡900/05·88	296	48·9	—	—	—	27·5	—
§900/11·76	276	31·1	—	—	—	34·8	—

* In *N*/8-solution. † 16 Hours. ‡ 7 Litres per hour. § 14 Litres per hour.

It must be admitted that the evidence for these changes from one charcoal to another with oxidation is not decisive. Further work is needed which should be sufficiently accurate to permit an examination of the k and $1/n$ curves in detail—an examination not warranted by the accuracy of the present work, which has, however, fixed the general shape of the curves with considerable certainty.

Summary.

A large quantity of wood charcoal has been prepared and mixed so as to give a substantially uniform product.

Some 80 samples have been oxidised by oxygen–nitrogen mixtures under regulated conditions. The following properties of the oxidised charcoals have been determined: Appearance, bulk density, percentage yield, sorptive capacity for iodine in benzene solution, and rate of sorption.

Sorption isotherms have been determined for 22 and for 150

Iodine in benzene solution : 150 hours' shaking.
Percentage change in normality at various concentrations.

Charcoal No.	*N*/50.	*N*/20.	*N*/10.	*N*/5.	Charcoal No.	*N*/50.	*N*/20.	*N*/10.	*N*/5.
500/00·01	49·4	36·6	26·7	16·4	700/12·39	85·6	57·2	38·2	23·8
500/00·25	47·1	34·8	26·1	16·7	700/18·14	85·7	58·0	40·2	25·5
500/01·13	43·7	33;9	25·9	16·5					
500/02·14	44·2	36·6	27·6	17·8	800/00·01	61·6	47·8	29·4	19·5
500/07·01	48·6	40·3	29·2	18·6	800/00·35	83·3	52·7	33·2	20·3
500/12·50	—	38·9	29·5	17·7	800/00·76	79·4	55·4	36·4	21·3
500/23·63	58·1	39·7	27·7	18·5	800/01·13	75·5	51·4	34·3	20·3
					800/01·49	70·9	51·6	33·1	19·2
600/00·01	74·2	60·2	35·1	19·7	800/02·77	85·5	56·7	37·7	23·9
600/00·06	77·5	56·4	36·8	20·5	800/03·57	84·9	57·8	38·7	24·9
600/00·59	80·0	57·2	37·0	20·7	800/06·91	—	63·9	43·5	29·0
600/01·40	70·9	55·4	35·6	20·5	800/15·48	88·1	68·3	46·7	31·7
600/02·35	69·0	41·5	31·5	18·3					
600/03·53	75·5	46·8	30·7	18·4	850/00·01	72·3	59·3	39·6	22·5
600/10·29	76·4	—	29·7	17·1	850/00·09	61·8	39·4	26·3	17·5
600/14·33	80·8	51·5	32·6	20·8	850/00·59	69·6	40·9	30·7	17·5
600/20·58	80·3	51·7	34·0	21·4	850/03·05	85·4	58·7	39·7	26·0
					850/04·45	84·8	57·8	39·1	25·5
700/00·01	91·4	59·6	38·2	21·3					
700/00·39	82·7	62·5	39·5	22·9	900/00·01	14·8	8·6	5·8	3·8
700/00·92	79·8	59·1	36·9	21·8	900/00·59	33·0	19·8	13·2	8·9
700/01·74	81·0	53·9	33·6	20·0	900/01·03	55·2	33·2	22·1	14·0
700/02·14	81·9	51·3	32·7	19·6	900/03·52	72·5	45·0	30·4	20·3
700/04·22	81·5	52·1	33·5	20·7	900/05·88	79·1	52·3	36·1	22·1
700/09·49	84·6	55·9	36·4	23·2	900/10·29	89·7	61·4	42·0	27·6

Adsorption of iodine from benzene solution.

Freundlich constants.

Charcoal No.	22 hours' shaking.		150 hours' shaking.		Charcoal No.	22 hours' shaking.		150 hours' shaking.	
	1/*n*.	*k*.	1/*n*.	*k*.		1/*n*.	*k*.	1/*n*.	*k*.
600/00·01	—	—	0·126	156	800/01·13	0·333	42·3	0·239	71·0
600/00·06	—	—	0·187	108	800/01·49	0·237	73·3	0·218	79·4
600/00·59	—	—	0·182	112	800/02·77	0·231	80·9	0·255	73·5
600/01·40	—	—	0·197	97·7	800/03·57	0·240	81·3	0·274	66·1
600/02·35	0·420	20·3	0·328	34·3	800/06·91	0·249	85·7	0·288	72·9
600/03·53	0·332	36·3	0·259	55·0	800/08·84	0·260	80·2	—	—
600/10·29	0·240	64·3	0·250	53·9	800/12·50	0·281	79·1	—	—
600/14·33	0·235	73·3	0·251	64·1	800/15·48	0·279	79·4	0·314	66·5
600/20·58	0·238	74·3	0·263	61·4					
					850/00·01	0·298	44·1	0·208	100
700/00·01	0·150	158	0·172	124	850/00·09	0·384	22·6	0·340	28·1
700/00·20	0·296	63·5	—	—	850/00·59	0·372	25·2	0·309	37·3
700/00·39	0·324	53·3	0·191	115	850/03·05	0·250	74·1	0·283	65·6
700/00·92	0·332	50·0	0·189	108	850/04·45	0·252	74·5	0·283	63·8
700/01·74	0·296	53·1	0·215	82·0	850/05·67	0·254	75·5	—	—
700/02·14	0·282	54·3	0·221	75·7					
700/04·22	0·270	58·9	0·242	69·3	900/00·01	0·444	2·28	0·396	3·85
700/09·49	0·256	69·8	0·257	69·6	900/00·22	0·411	6·31	—	—
700/12·39	—	—	0·257	72·9	900/00·59	0·355	11·0	0·377	10·3
700/18·14	0·293	63·4	0·283	65·8	900/01·03	0·300	29·2	0·350	21·0
700/21·06	0·295	62·7	—	—	900/02·35	0·265	46·6	—	—
					900/03·52	0·260	57·7	0·310	40·1
800/00·01	—	—	0·268	52·0	900/05·88	0·255	70·0	0·292	53·0
800/00·35	0·261	63·8	0·227	75·9	900/10·29	0·246	85·3	0·267	77·3
800/00·76	0·328	46·0	0·220	86·1	900/14·70	0·253	90·6	—	—

hours' shaking for each oxidised charcoal over a range of concentration from $N/100$- to $N/5$-iodine in benzene.

An ageing effect has been observed.

The isotherms are mostly parabolic. Their Freundlich constants have been plotted against degree of oxidation of the charcoal for five different temperatures. A study of these curves has led to suggestions explaining the changes in the charcoal with progressive oxidation. These suggestions are based on the views of Philip, Dunnill, and Workman, and of Chaney.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CC.—*The Heat of Adsorption of Gases by Charcoal.*

By SIDNEY JOHN GREGG.

AN examination of the literature dealing with the theories of the adsorption of gases by charcoal showed that one particular experimental quantity—the heat of adsorption—is especially important in testing them; and since the relevant data are very scanty, the following series of experiments was undertaken in order to measure this quantity, together with the more usual ones, equilibrium pressure and amount adsorbed. Measurements were therefore carried out at 0° with the aid of a Bunsen ice calorimeter, and also at 40° using the same calorimeter filled with phenol instead of ice. The adsorption of eight different gases on a standard charcoal was studied, and also the adsorption of a given gas on several different charcoals.

EXPERIMENTAL.

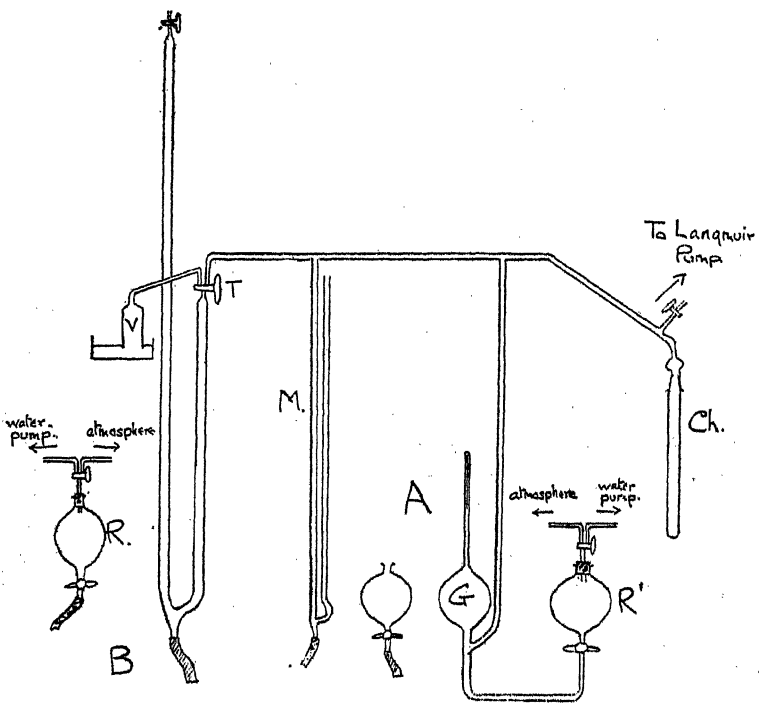
The apparatus (Fig. 1) consists of two main parts, the gas burette, B, and the adsorption system, A, sealed together and mounted on a board, which can slide vertically, thus allowing the charcoal tube, Ch, to be lowered into the calorimeter.

The gas burette is a modification of that used in the Bone–Wheeler gas-analysis apparatus. The gas to be measured is drawn from the reservoir, V, where it is stored over mercury, into the shorter limb of the burette *via* the three-way tap, T. Since a Torricellian vacuum (produced by previous sweeping out of the air) exists above the mercury in the longer limb, the pressure of the gas in the shorter limb is given directly by the difference of mercury levels in the two limbs. The volume of the gas is known from the calibration figures

for the shorter limb, and its temperature is also known, so that the quantity of gas can be calculated. It can then be admitted to the adsorption system by means of the tap T.

The adsorption system consists of an ordinary open tube manometer, M, a McLeod gauge, G, and the charcoal tube, which is joined to the rest of the apparatus by a ground glass joint. The McLeod gauge is joined to its mercury reservoir, R′, by an all-glass connexion, the raising or lowering of the mercury levels in this case, as also with

FIG. 1.



the gas burette, being accomplished by applying atmospheric pressure or a water-pump vacuum, respectively, to the space above the mercury in the reservoir.

The ice calorimeter is of the usual type, but is fitted with an outer jacket which can be evacuated by means of a Langmuir pump. A simple Geissler tube connected with this jacket gives a ready means of testing the vacuum from time to time, and whenever this falls much below *X*-ray hardness, the jacket must be re-evacuated. This jacket, in conjunction with a very large and amply lagged bath of ice (diameter, 14 inches; depth, 16 inches) from which the water

was frequently siphoned off, made it possible normally to obtain a leak of only 0·02 or 0·03 calorie per hour, though on occasions it rose much higher than this.

The desirability of measuring the heat of adsorption at a temperature other than 0° led to the attempt to use other working substances in the Bunsen calorimeter. Owing to the difficulty of keeping a thermostat sufficiently constant at the m. p. of anethole (19·5°), this substance was not satisfactory (compare Grassi, *Atti R. Accad. Lincei*, 1913, **22**, I, 304), but ultimately phenol was found to be a fairly suitable substitute. For accurate working, the normal heat leaks from the surroundings of the calorimeter should be constant enough to produce a small and steady creep of the mercury meniscus in the capillary in one direction; actually, it was found that a bath showing no variation on a Beckmann thermometer still gave unsteady heat leaks, and even in the best cases the mercury meniscus oscillated in the capillary over a range of some 0·6 cm., so that the readings are always uncertain to at least this extent. This is, unfortunately, an appreciable fraction of the movement due to the heat of adsorption itself, which was usually of the order of 10 cm. at each reading. In order to achieve even this degree of success, it was necessary to have very rapid stirring of the bath, to employ a large thermo-regulator, and to cover the top of the bath to minimise irregular evaporation.

Calibration of the Calorimeters.—The standard figure 1 cal. $\equiv$ 0·001132 c.c. was adopted for the ice calorimeter. The phenol calorimeter was calibrated by an electrical method, a known quantity of electrical energy being passed through a heating coil immersed in mercury, contained in the reaction tube of the calorimeter. The coil was of nichrome wire, welded on to copper leads, and was rendered insulating by momentary heating in a Bunsen flame, whereby a coating was formed on it such that on immersion in mercury it suffered no reduction in resistance. A voltmeter was connected across the terminals, and a known current passed for a definite period, the change in volume of the phenol being read on the capillary. A mean of several determinations gave 1 cal. $\equiv$ 0·00169 $\pm$ 0·00002 c.c. Finally, the temperature of operation was found to be 40·35° by immersing a standard thermometer in mercury contained in the reaction tube.

Charcoals.—A stock of charcoal was prepared by heating small cubes of birch wood in a large silica test tube in an electric furnace for 4 hours at about 400°. Four different samples were then prepared by activating separate charges of the stock at different temperatures in a very slow stream of nitrogen (containing 0·5% of oxygen). Details of these are :

Charcoal No.	I	II	III	IV
Time of activation (hrs.)	3	4	4	3
Temp. of activation	600°	800°	500°	450°

Manipulation.—The charcoal was dried in a vacuum desiccator for 5 hours, and 3—5 g. were accurately weighed into the charcoal tube, which was then placed in position on the adsorption apparatus and surrounded by an electric furnace. The charcoal was then evacuated by a mercury condensation pump for 24 hours, its temperature being maintained at 400°, as read by a pyrometer whose junction was in contact with the bottom of the charcoal tube. At the end of this time the pressure was of the order 0·0001 mm., and on cooling, it always became so low as to be unreadable. By means of the sliding board, the charcoal tube was now lowered into the reaction tube of the calorimeter, into which mercury was poured in order to facilitate heat conduction from the charcoal to the calorimeter during the subsequent measurements; to prevent heat losses by convection from the top of the reaction tube, the space between this and the charcoal tube was covered with a piece of plasticine. As soon as the movement in the capillary became constant, the first charge of gas was admitted, and readings of the pressure were taken every few minutes until two consecutive readings were identical, showing that equilibrium had been reached. When the calorimeter was working well, it was possible to use the heat readings as a check on the attainment of equilibrium, for when the creep became the same as before the admission of gas, one could assume that equilibrium had been reached.

The sorption curve was obtained by adding successive small quantities of gas from the burette, as outlined above, whilst, in order to obtain the desorption curve, the burette was opened to the adsorption system, thus enlarging the volume of the dead space. After a minute or so, the burette was shut off, the volume of gas withdrawn was read, and the attainment of equilibrium awaited.

In most cases, fresh samples of charcoal were used for each experiment. In a few instances, however, the supply of fresh charcoal was insufficient, and on these occasions, samples of charcoal that had been used for previous experiments had to be employed; in order to reduce the activating effect in such cases to a minimum, the charcoals were freed from gas at a lower temperature than before, *viz.*, at 150°, and in some cases even at room temperature. Nevertheless, as will be explained later, a small activating effect was still present, the charcoal being slightly altered during each removal of gas.

Calculations.—In calculating volumes of gas, correction is made for the deviation from Boyle's law, and the volume which would be

occupied ideally by the gas at *N.T.P.* thus obtained. To calculate the amount of gas v_a that has been adsorbed up to a given reading, the amount v_u remaining unadsorbed in the dead space is subtracted from the total amount v_i which has been admitted to the system; in calculating v_u, it must be remembered that part of the dead space is at room temperature and part at that of the calorimeter. In order to obtain the heat of adsorption corresponding to a given charge of gas, a correction must be made for the heat communicated to the calorimeter by the gas when changing from room temperature to 0° or 40·35° as the case may be. This correction is $v_c s(t_1 - t_2)$, where s is the specific heat of the gas per c.c. at constant volume, and v_c is the amount of gas that has been changed from the temperature of the atmosphere, t_1, to that of the calorimeter, t_2.

Degree of Accuracy.—No attempt has been made to attain to any great degree of accuracy for two main reasons: (i) Charcoal itself is such an indefinite substance, and is so difficult to obtain in a perfectly homogeneous condition, that excessive accuracy in the measurements would be superfluous; and (ii) the accuracy attainable with the ice calorimeter is not so high as to justify great accuracy in the measurement of the other two quantities. A rough estimate of the probable error of the respective measurements is as follows:

Pressure: Never greater than $\pm$ 1%, and for higher pressures (10 cm. or more), of the order $\pm$ 0·2%.

Amount adsorbed: Between $\pm$ 0·5% and $\pm$ 1·0%.

Heat: Very variable, but of the order $\pm$ 2% for the ice-, and $\pm$ 5% for the phenol-calorimeter.

Note on the Purity of the Gases.—In these experiments, the fact that hysteresis (see "Discussion") was absent, was assumed to prove that the gas was pure, since the presence of air as an impurity immediately produced the phenomenon. The author has since recognised that this is inadequate evidence of purity, however, for the work of Lorenz and Wiedbrauck (*Z. anorg. Chem.*, 1925, **143**, 268) indicates that only when gases differ widely in physical properties do they interfere with each other's adsorption. Hence the absence of hysteresis does not necessarily indicate the absence of impurities similar in physical properties to the gas in question; such impurities, however, would have but a very slight effect on the adsorption measurements.

Results.

The following quantities are given for each reading:

x = total number of g.-mols. of gas adsorbed per g. of charcoal ($= v_a/22414\,w$, where w is the weight of charcoal).

p = equilibrium pressure (cm. of Hg).

Q = integral heat of adsorption per g. of charcoal, $= \Sigma h$, where h is the amount of heat evolved per g. of charcoal at a given reading.

In the curves, desorption points are denoted by a small tail attached to the circle, etc., which surrounds the point, thus ⊙.

Experiment 1 : Nitrous oxide + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·383	$\bar{1}$·715	0·280	$\bar{3}$·294	1·351	1·160	$\bar{3}$·433	1·764	1·284
$\bar{4}$·669	0·106	0·557	$\bar{3}$·337	1·464	1·195	$\bar{3}$·413	1·677	1·264
$\bar{4}$·861	0·405	0·754	$\bar{3}$·373	1·582	1·227	$\bar{3}$·383	1·596	1·238
$\bar{4}$·992	0·662	0·871	$\bar{3}$·406	1·684	1·255	$\bar{3}$·335	1·411	1·193
$\bar{3}$·097	0·873	0·981	$\bar{3}$·432	1·781	1·281	$\bar{3}$·282	1·259	1·145
$\bar{3}$·173	1·073	1·057	$\bar{3}$·456	1·862	1·305	$\bar{3}$·242	1·151	1·106
$\bar{3}$·240	1·224	1·114						

Preparation of gas. Sodium nitrite solution was slowly dropped into warm hydroxylamine hydrochloride solution, and the nitrous oxide evolved was passed in succession through potassium hydroxide solution, over solid potassium hydroxide, through concentrated sulphuric acid, and finally over phosphorus pentoxide.

Experiment 1*a* : Nitrous oxide + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·714	0·173	0·560	$\bar{3}$·345	1·461	1·159	$\bar{3}$·405	1·665	1·209
$\bar{3}$·085	0·834	0·905	$\bar{3}$·416	1·706	1·222	$\bar{3}$·349	1·473	1·155
$\bar{3}$·255	1·216	1·075	$\bar{3}$·449	1·839	1·250			

Charcoal. The charcoal from Expt. 1 was freed from gas at room temperature without intermediate exposure to air.

Preparation of gas. As for Expt. 1.

Experiment 2 : Nitrous oxide + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·434	$\bar{1}$·734	0·161	$\bar{3}$·247	1·152	1·060	$\bar{3}$·460	1·840	1·259
$\bar{4}$·744	0·167	0·557	$\bar{3}$·322	1·360	1·136	$\bar{3}$·485	1·944	1·267
$\bar{4}$·936	0·498	0·759	$\bar{3}$·364	1·486	1·176	$\bar{3}$·446	1·793	1·244
$\bar{3}$·055	0·736	0·884	$\bar{3}$·395	1·590	1·207	$\bar{3}$·393	1·579	1·175
$\bar{3}$·163	0·951	0·978	$\bar{3}$·428	1·722	1·241			

Preparation of gas. After being prepared as in Expt. 1, it was liquefied by cooling in liquid air, and then distilled in a vacuum.

Experiment 3 : Nitrous oxide + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·803	0·281	0·657	$\bar{3}$·360	1·493	1·216
$\bar{3}$·288	1·274	1·148	$\bar{3}$·415	1·671	1·264

Preparation of gas. As in Expt. 2.

Experiment 4 : Acetylene + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·494	$\bar{1}$·537	0·458	$\bar{3}$·328	1·298	1·250	$\bar{3}$·438	1·790	1·351
$\bar{4}$·798	0·034	0·749	$\bar{3}$·375	1·480	1·290	$\bar{3}$·417	1·667	1·338
$\bar{4}$·995	0·412	0·922	$\bar{3}$·412	1·644	1·323	$\bar{3}$·370	1·454	1·295
$\bar{3}$·167	0·809	1·081	$\bar{3}$·441	1·797	1·349	$\bar{3}$·305	1·202	1·238
$\bar{3}$·254	1·051	1·179	$\bar{3}$·462	1·915	1·370	$\bar{3}$·227	0·952	1·155

Preparation of gas. Water was dropped on calcium carbide in an evacuated apparatus, and the acetylene was passed through saturated potassium permanganate solution, over solid potassium hydroxide and phosphorus pentoxide, then solidified and redistilled in a high vacuum.

Experiment 5 : Ethane + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·524	$\bar{1}$·282	0·505	$\bar{3}$·197	0·467	1·150	$\bar{3}$·416	1·425	1·361
$\bar{4}$·866	$\bar{1}$·785	0·831	$\bar{3}$·313	0·874	1·258	$\bar{3}$·444	1·638	1·386
$\bar{4}$·053	0·070	1·013	$\bar{3}$·373	1·146				

Preparation of gas. Propionitrile was dropped on sodium wire in an evacuated apparatus (see Stähler *et al.*, " Arbeitsmethoden der Anorganischen Chemie," 1926, IV, p. 93), and the ethane passed in succession through tubes containing the following reagents : potassium hydroxide solution, solid potassium hydroxide, concentrated sulphuric acid, and phosphorus pentoxide. It was then solidified and redistilled in high vacuum. The presence of hysteresis showed that the gas was not pure, although Cardoso and Bell (*J. Chim. physique*, 1912, **10**, 498) endorse the method as giving pure ethane.

Remark. The attainment of equilibrium at some readings required several hours, again indicating that the gas was not pure.

Experiment 6 : Carbon monoxide + Charcoal I at 0°.

log x.	log p.	log x.	log p.	log x.	log p.	log x.	log p.
$\bar{5}$·973	0·845	$\bar{4}$·521	1·494	$\bar{4}$·753	1·831	$\bar{4}$·576	1·566
$\bar{4}$·199	1·098	$\bar{4}$·588	1·582	$\bar{4}$·824	1·920	$\bar{4}$·444	1·388
$\bar{4}$·403	1·339	$\bar{4}$·686	1·723	$\bar{4}$·709	1·754	$\bar{4}$·176	1·065

Preparation of gas. Concentrated sulphuric acid was dropped on sodium formate, and the gas passed through tubes of potassium hydroxide solution, solid potassium hydroxide, and phosphorus pentoxide. The apparatus was alternately evacuated and filled with carbon monoxide three times before the gas was collected.

Experiment 7 : Sulphur dioxide + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{3}$·210	$\bar{1}$·330	1·287	$\bar{3}$·606	1·517	1·655	$\bar{3}$·589	1·263	1·639
$\bar{3}$·495	0·430	—	$\bar{3}$·623	1·708	1·669	$\bar{3}$·567	1·072	1·624
$\bar{3}$·567	1·013	1·621	$\bar{3}$·606	1·467	1·653	$\bar{3}$·531	0·722	1·597
$\bar{3}$·590	1·367	1·645						

Preparation of gas. Sulphur dioxide from a cylinder was passed through tubes of concentrated sulphuric acid and phosphorus pentoxide. It was then solidified and redistilled in a high vacuum.

Experiment 8 : Carbon dioxide + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·315	$\bar{1}$·844	0·212	$\bar{3}$·162	1·183	1·016	$\bar{3}$·432	1·910	1·272
$\bar{4}$·573	0·201	0·455	$\bar{3}$·238	1·360	1·083	$\bar{3}$·450	1·984	1·293
$\bar{4}$·811	0·555	0·680	$\bar{3}$·299	1·522	1·145	$\bar{3}$·408	1·833	1·252
$\bar{4}$·948	0·779	0·810	$\bar{3}$·354	1·654	1·194	$\bar{3}$·360	1·657	1·199
$\bar{3}$·066	0·989	0·921	$\bar{3}$·408	1·820	1·246	$\bar{3}$·305	1·493	1·146

Preparation of gas. Concentrated sulphuric acid was dropped on solid sodium carbonate in an evacuated apparatus. The gas was dried by concentrated sulphuric acid and phosphorus pentoxide, solidified, and redistilled in a vacuum.

Experiment 9 : Ethylene + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·280	$\bar{1}$·071	0·187	$\bar{3}$·298	1·345	1·130	$\bar{3}$·347	1·589	1·170
$\bar{4}$·537	$\bar{1}$·452	0·444	$\bar{3}$·333	1·545	1·165	$\bar{3}$·304	1·346	1·131
$\bar{4}$·765	$\bar{1}$·822	0·652	$\bar{3}$·363	1·713	1·188	$\bar{3}$·247	1·201	1·104
$\bar{4}$·945	0·195	0·811	$\bar{3}$·383	1·846	1·206	$\bar{3}$·183	0·945	1·049
$\bar{3}$·063	0·513	0·917	$\bar{3}$·396	1·953	1·218	$\bar{3}$·101	0·647	0·972
$\bar{3}$·163	0·805	1·010	$\bar{3}$·377	1·790	1·198	$\bar{4}$·957	0·245	0·842
$\bar{3}$·237	1·074	1·074						

Preparation of gas. A mixture of 50 c.c. each of concentrated sulphuric acid and absolute alcohol was placed in a distilling flask, and a little sand (previously washed with concentrated hydrochloric acid and ignited) was added. A mixture of 50 c.c. of concentrated sulphuric acid with 25 c.c. of absolute alcohol was slowly added from a dropping funnel, the flask being warmed. The whole apparatus was previously evacuated. The ethylene was passed successively through tubes containing solid potassium hydroxide, concentrated sulphuric acid, and phosphorus pentoxide; it was then solidified and redistilled in a vacuum.

Experiment 9*a* : Ethylene + Charcoal I at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·818	0·000	0·665	$\bar{3}$·301	1·396	1·114	$\bar{3}$·341	1·599	1·148
$\bar{3}$·132	0·730	0·955	$\bar{3}$·376	1·831	1·184	$\bar{3}$·292	1·325	1·104

Charcoal. The charcoal from Expt. 9 was freed from gas at room temperature without intermediate exposure to air.

Preparation of gas. As for Expt. 9.

Experiment 10 : Nitrogen + Charcoal I at 0°.

log x.	log p.	log x.	log p.	log x.	log p.	log x.	log p.
$\bar{5}$·578	0·656	$\bar{4}$·260	1·398	$\bar{4}$·573	1·790	$\bar{4}$·238	1·376
$\bar{5}$·971	1·073	$\bar{4}$·391	1·554	$\bar{4}$·646	1·884	$\bar{4}$·095	1·188
$\bar{4}$·168	1·291	$\bar{4}$·492	1·684	$\bar{4}$·564	1·777	$\bar{5}$·935	1·002

Preparation of gas. Nitrogen from a cylinder was used; it contained 0·5% of oxygen.

The gases used in the remaining experiments were prepared as described in the corresponding preceding experiments.

Experiment 11 : Nitrous oxide + Charcoal II at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·573	$\bar{1}$·872	0·498	$\bar{3}$·215	1·005	1·103	$\bar{3}$·442	1·637	1·312
$\bar{4}$·893	0·389	0·806	$\bar{3}$·314	1·252	1·194	$\bar{3}$·474	1·752	1·342
$\bar{3}$·103	0·757	0·997	$\bar{3}$·390	1·473	1·265	$\bar{3}$·503	1·864	1·370

Experiment 12 : Sulphur dioxide + Charcoal II at 0°.

$\bar{4}$·685	$\bar{2}$·633	0·755	$\bar{3}$·620	1·412	1·639	$\bar{3}$·642	1·559	1·657
$\bar{3}$·084	$\bar{1}$·124	1·133	$\bar{3}$·638	1·660	1·652	$\bar{3}$·626	1·344	1·643
$\bar{3}$·405	$\bar{1}$·935	1·425	$\bar{3}$·651	1·834	1·665	$\bar{3}$·611	1·148	1·623
$\bar{3}$·511	0·398	1·522	$\bar{3}$·659	1·923	1·672	$\bar{3}$·599	1·985	1·609
$\bar{3}$·584	0·969	1·601	$\bar{3}$·650	1·683	1·662	$\bar{3}$·585	0·848	1·598

Charcoal. This charcoal had been previously used for Expt. 11 and was freed from gas at room temperature.

Experiment 13 : Nitrogen + Charcoal II at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·121	1·139	$\bar{1}$·761	$\bar{4}$·645	1·781	0·301	$\bar{4}$·653	1·774	0·305
$\bar{4}$·387	1·446	0·041	$\bar{4}$·712	1·892	0·387	$\bar{4}$·577	1·663	0·240
$\bar{4}$·539	1·641	0·196	$\bar{4}$·780	1·969	0·433			

Experiment 14 : Nitrous oxide + Charcoal III at 0°.

$\bar{4}$·610	0·137	0·318	$\bar{3}$·277	1·406	1·003	$\bar{3}$·380	1·752	1·101
$\bar{4}$·912	0·610	0·617	$\bar{3}$·331	1·577	1·061	$\bar{3}$·352	1·647	1·067
$\bar{3}$·094	0·955	0·802	$\bar{3}$·373	1·725	1·104	$\bar{3}$·328	1·562	1·041
$\bar{3}$·204	1·209	0·921	$\bar{3}$·405	1·856	1·133	$\bar{3}$·308	1·477	1·015

Charcoal. This had been previously used for Expt. 15 and was freed from gas at room temperature.

Remark. The calorimeter was working very badly during this experiment, and the heat measurements are therefore untrustworthy.

Experiment 15 : Sulphur dioxide + Charcoal III at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·960	$\bar{2}$·875	1·040	$\bar{3}$·552	1·109	1·575	$\bar{3}$·633	1·881	1·654
$\bar{3}$·270	$\bar{1}$·432	—	$\bar{3}$·582	1·396	1·606	$\bar{3}$·612	1·680	1·641
$\bar{3}$·442	0·272	1·485	$\bar{3}$·604	1·605	1·625	$\bar{3}$·590	1·478	1·621
$\bar{3}$·507	0·705	1·540	$\bar{3}$·620	1·759	1·641	$\bar{3}$·570	1·298	1·613

Experiment 16 : Nitrogen + Charcoal III at 0°.

log x.	log p.	log x.	log p.	log x.	log p.	log x.	log p.
$\bar{5}$·882	1·195	$\bar{4}$·363	1·738	$\bar{4}$·397	1·753	$\bar{4}$·056	1·355
$\bar{4}$·206	1·547	$\bar{4}$·488	1·877	$\bar{4}$·272	1·604		

Charcoal. This had been used for Expts. 14 and 15 and was freed from gas at room temperature.

Experiment 17 : Sulphur dioxide + Charcoal IV at 0°.

log x.	log p.	log Q.	log x.	log p.	log Q.	log x.	log p.	log Q.
$\bar{4}$·606	$\bar{2}$·484	0·740	$\bar{3}$·477	0·968	1·510	$\bar{3}$·588	1·621	1·597
$\bar{3}$·059	$\bar{1}$·441	1·143	$\bar{3}$·545	1·377	1·562	$\bar{3}$·559	1·437	1·573
$\bar{3}$·261	$\bar{1}$·828	1·321	$\bar{3}$·590	1·674	1·592	$\bar{3}$·496	1·008	1·536
$\bar{3}$·382	0·389	1·426	$\bar{3}$·622	1·856	1·614			

Experiment 18 : Nitrous oxide + Charcoal I at 40·35°.

$\bar{4}$·551	0·668	0·484	$\bar{3}$·039	1·467	0·956	$\bar{3}$·190	1·729	1·078
$\bar{4}$·781	1·007	0·708	$\bar{3}$·096	1·571	1·010	$\bar{3}$·139	1·623	1·036
$\bar{4}$·882	1·184	0·805	$\bar{3}$·178	1·733	1·090	3·093	1·525	1·996
$\bar{4}$·962	1·346	0·889	$\bar{3}$·235	1·856	1·144			

Experiment 19 : Sulphur dioxide + Charcoal I at 40·35°.

$\bar{4}$·589	$\bar{1}$·459	0·837	$\bar{3}$·451	1·285	1·561	$\bar{3}$·430	1·035	1·531
$\bar{4}$·855	$\bar{1}$·931	1·085	$\bar{3}$·504	1·607	1·599	$\bar{3}$·398	0·743	1·497
$\bar{3}$·157	0·338	1·306	$\bar{3}$·490	1·476	1·586	$\bar{3}$·332	0·310	1·447
$\bar{3}$·288	0·650	1·422	$\bar{3}$·451	1·184	1·550	$\bar{3}$·206	0·272	1·338
$\bar{3}$·387	0·969	1·505						

Charcoal. This had been previously used for Expt. 6, and was freed from gas at 150°.

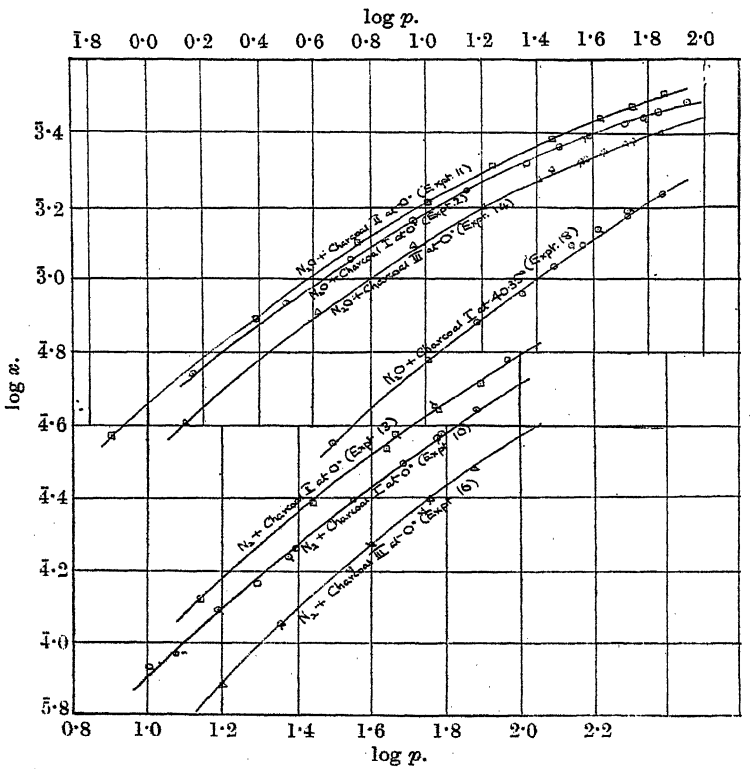
Discussion.

During the earlier stages of the work, great trouble was experienced from the occurrence of "hysteresis," which is a well-known phenomenon in adsorption work; the desorption curve, obtained by withdrawing the gas from the charcoal, does not retrace the sorption curve, the charcoal always retaining more gas for a given pressure on the curve of desorption than on that of sorption. Furthermore, the time required to attain equilibrium is much shorter (of the order of one hour) during desorption than during sorption, in which the pressure may continue to fall for several days. In agreement with Patrick (*J. Amer. Chem. Soc.*, 1920, **42**, 946) and others, the trouble was found to be due to traces of non-condensable gas in the system; for when the gas to be adsorbed was liquefied and then distilled in high vacuum, and when the charcoal was thoroughly evacuated, the sorption and desorption curves could be made to agree, and the time for equilibrium in both cases became normal at about one hour. Only with ethyl chloride was this treatment ineffective, for no matter how carefully the gas was prepared, considerable hysteresis was observed; hence adsorption experiments with this gas were abandoned.

As has been shown by many previous workers, neither the p–x nor the log p–log x curve possesses a simple analytical form; the shape of the latter curve does not even appear to bear any simple relationship to the nature of the adsorbed gas, though it must be remembered that it is difficult to give criteria for selecting comparable parts of the curve for different gases; thus, while the sulphur dioxide curve

at atmospheric pressure is approaching the point of saturation, the curve for a permanent gas like nitrogen is still in its early stages. On the other hand, the log p–log x curves undergo a regular variation with the change of charcoal, for the order of the curves for the charcoals I, II, and III is the same for the three widely different gases nitrogen, nitrous oxide, and sulphur dioxide—charcoal II always having the greatest adsorption for a given pressure, charcoal

FIG. 2.



I the next, and charcoal III the smallest. This is illustrated for nitrogen and nitrous oxide by the curves in Fig. 2.

Q and x are connected by the simple relation $Q = kx^n$, where k and n are constants at constant temperature, a result obtained also by other workers (*e.g.*, Lamb and Coolidge, *J. Amer. Chem. Soc.*, 1920, **42**, 1146). The index n is roughly characteristic of the gas which is adsorbed, for, as will be seen from Table I, it remains approximately constant when one gas is adsorbed on different charcoals, and varies from gas to gas for the same charcoal. The

rule is only a rough one, however, for in some cases quite a large difference is obtained for the same gas. This is illustrated by sulphur dioxide with charcoals I and IV (Expts. 7 and 17, respectively).

FIG. 3.

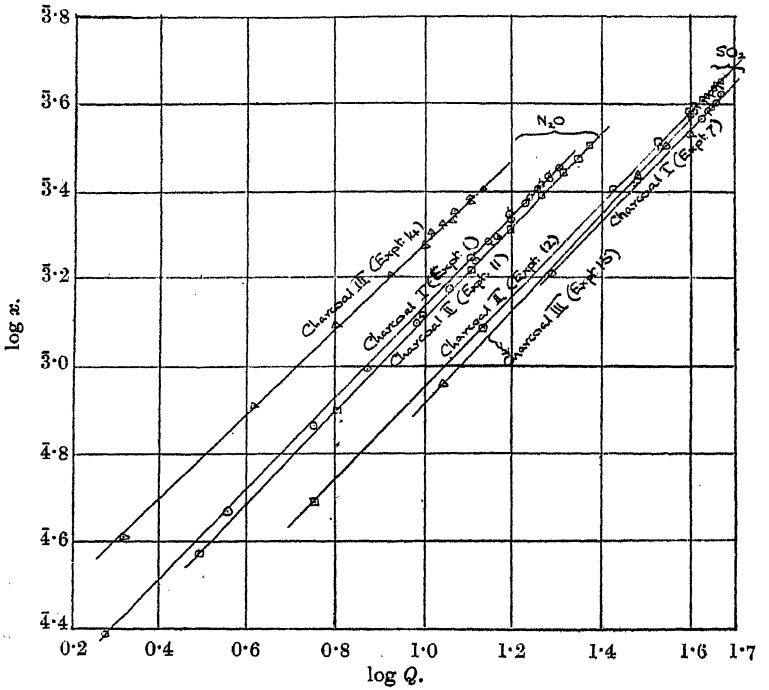


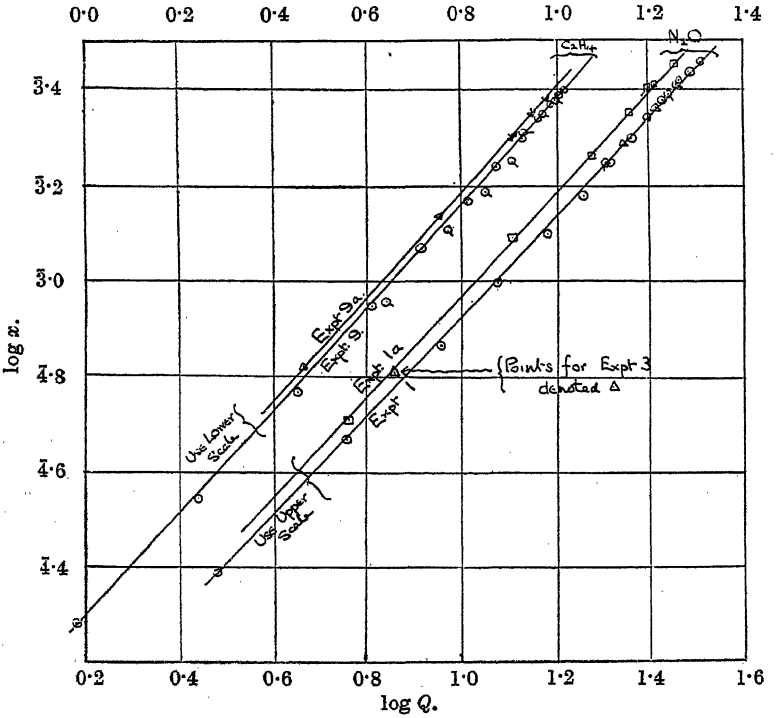
TABLE I.

Values of k and n in the formula $Q = kx^n$.

Temp.	Expt. No.	Gas.	Charcoal.	n.	log k.
0°	1	N_2O	I	0·940	3·703
	1*a*	,,	I	0·940	3·651
	3	,,	I	0·953	3·726
	11	,,	II	0·933	3·706
	14	,,	III	1·01 (?)	3·745 (?)
40·35°	18	,,	I	0·957	3·695
0°	7	SO_2	I	0·915	3·843
	12	,,	II	0·942	3·877
	15	,,	III	0·911	3·811
	17	,,	IV	0·885	3·746
40·35°	19	,,	I	0·840	3·695
0°	4	C_2H_2	I	0·945	3·770
	5	C_2H_6	I	0·966	3·963
	8	CO_2	I	0·955	3·726
	9	C_2H_4	I	0·924	3·627
	9*a*	,,	I	0·926	3·613
	13	N_2	II	1·005	3·676

The data available are too limited to decide whether any simple rule holds for the variation of k; for the nitrous oxide experiments, the log Q–log x curves are in the same order as the corresponding isotherms—charcoal II having the largest k, charcoal I the next, and charcoal III the smallest (see Fig. 3). It is difficult, however, to pronounce judgment upon the apparently anomalous order of the sulphur dioxide curves, for they lie so close together that a small experimental error would alter their relative order; it is possible that

FIG. 4.



such an error may be present in the experiment with charcoal II, for the abnormally high value of n in this case throws doubt on the accuracy of the curve.

*It is here appropriate to note the effect of the adsorption of one gas upon the subsequent adsorption of the same or a different gas by a given charcoal. In Fig. 4 are plotted the log Q–log x curves for ethylene on charcoal I, Expt. 9 being carried out with fresh charcoal, and Expt. 9*a* after pumping out the gas from the used charcoal at room temperature and without intermediate exposure to the atmosphere. The curves for Expts. 1 and 1*a* represent a similar

pair for nitrous oxide, and the curve for Expt. 3 was obtained with charcoal I that had been previously saturated with ammonia and evacuated at room temperature. It will be seen that a small de-activating effect is indicated in the heat curves in each case, the value of k being slightly decreased, though the corresponding log p–log x curves show no such effect.

The heat of adsorption should now be compared with the latent heat of condensation of the adsorbed gas. For this purpose, one must use the differential heat of adsorption, $dQ/dx = knx^{n-1}$, *i.e.*, the heat evolved per g.-mol. of gas, since this is the quantity comparable with the latent heat; and this must relate to a fixed value of x in each case.

Since n is always less than unity, the differential heat of adsorption decreases as the concentration increases, but its value can be calculated for a given value of x within the range of the experiments, *e.g.*, $x = 1000 \times 10^{-6}$ g.-mol. per g. of charcoal. From Table II it will be seen that this differential heat is in each case 2—3 times as large as the latent heat of condensation of the vapour at 0° (calculated by the Clausius–Clapeyron equation); this agrees with the results of Lamb and Coolidge (*loc. cit.*) for several organic vapours.

TABLE II.

Heats of adsorption and latent heats of condensation.

Gas.	Molecular latent heat (cal.).	dQ/dx (cal.) for $x = 1000 \times 10^{-6}$.
Sulphur dioxide	6,160	11,460
Ethylene	2,050	6,620
Acetylene	2,580	8,100
Carbon dioxide	2,570	6,930
Nitrous oxide	2,510	7,180
Nitrogen (Charcoal II)	—	4,740

(The charcoal used in the first five cases was No. I.)

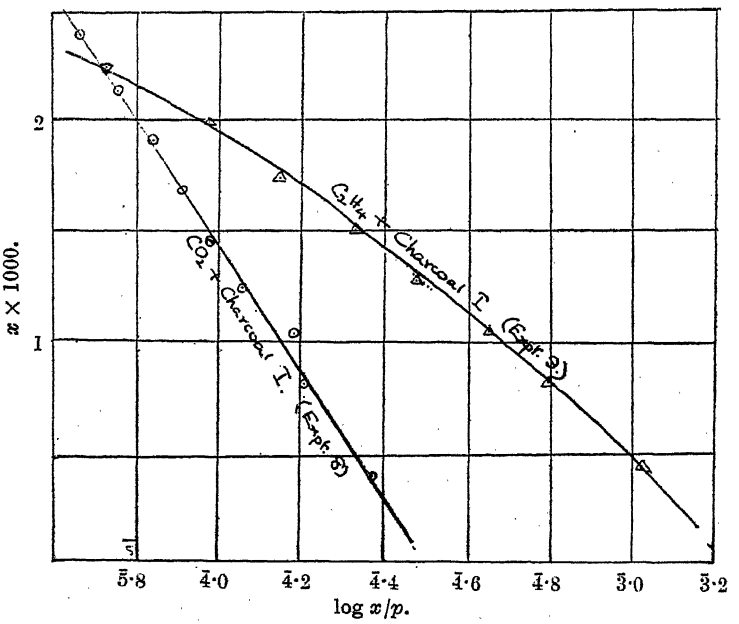
It is further of interest to compare the heat of adsorption of nitrous oxide at 0° with that at 40·35°, these temperatures being, respectively, below and above the critical temperature (35—39°). Whilst it must be borne in mind that, owing to the difficulty of working the phenol calorimeter, the measurements at 40·35° give little more than the order of magnitude of the heat of adsorption, yet it will be seen that the values of k and n at the two temperatures are not very different, showing that at a given concentration x, the integral heat of adsorption and the differential dQ/dx at the respective temperatures are also not very different.

This approximate constancy, with reference to temperature, of the heat effect of adsorption is confirmed by the fact that the value of the differential heat of adsorption calculated from the van't Hoff

isochore, on the assumption that it remains constant between 0° and 40·35°, is close to the experimental value. In the isochore $d \log_e K/dT = -H/RT^2$, where K is the equilibrium constant and H is the heat of reaction, K may be replaced by p, and integration then gives $\log_e p_1/p_2 = H(T_2 - T_1)/RT_1T_2$, where p_1 and p_2 are the equilibrium pressures at temperatures T_1 and T_2, respectively, for a given value of x, so that H becomes the differential heat of adsorption for the same value of x.

The values of $\log p$ for nitrous oxide on charcoal I at 0° (Expt. 2) and 40·35° (Expt. 18) are, respectively, 0·605 and 1·372 when

FIG. 5.



$x = 1000 \times 10^{-6}$; putting $T_1 = 273$, $T_2 = 313{\cdot}35$, and $R = 1{\cdot}98$, H is calculated to be 7442 cals. per g.-mol. per g. of charcoal. This is close to the value 7180 cal. obtained from the formula $dQ/dx = knx^{n-1}$ by using the experimental values of k and n for nitrous oxide at 0° on charcoal I (Expt. 1).

Although the p–x curve cannot be represented by any simple mathematical equation, the results agree fairly well with an equation of the form $\log x/p = A_0 - A_1x$, which has been deduced thermodynamically by Williams (*Proc. Roy. Soc.*, 1919, **96**, *A*, 287) and from kinetic theory by Henry (*Phil. Mag.*, 1922, **44**, 689). Thus on plotting $\log x/p$ against x (see Fig. 5), a straight line is obtained for

carbon dioxide, acetylene, nitrous oxide, carbon monoxide, or nitrogen with charcoal I; but deviations from the rectilinear occur in other cases, *e.g.*, ethylene and nitrogen with charcoals II and III, and also in Homfray's results (*Z. physikal. Chem.*, 1910, **74**, 129) for ethylene and nitrogen, and Richardson's (*J. Amer. Chem. Soc.*, 1917, **39**, 1828) for carbon dioxide. Furthermore, on plotting the results for sulphur dioxide from the present measurements, and also those for ammonia from Richardson's, the curves are not even approximately rectilinear. In general, however, it may be said that the Williams–Henry equation does reproduce moderately well the adsorption measurements at 0° for those gases which are far removed from their condensation point at *N.T.P.*; but, as it is hoped to show elsewhere, this fact is insufficient evidence for the validity of either Williams's or Henry's fundamental assumptions.

The values of the constants A_0 and A_1 for those cases where the equation holds are given in Table III. The equation put forward by Iljin (*Physikal. Z.*, 1925, **26**, 497) extends to the adsorption of

TABLE III.

Values of A_0 and A_1 in the equation $\log x/p = A_0 - A_1 x$.

Gas.	Charcoal.	A_1.	A_0.	Gas.	Charcoal.	A_1.	A_0.
N_2	I	525	−5·059	C_2H_2	I	510	−2·887
,,	II	410	−4·961	N_2O	I	410	−3·209
,,	III	388	−5·263	,,	II	400	−3·160
CO	I	432	−4·832	,,	III	375	−3·360
CO_2	I	355	−4·490	,, (40°)	I	370	−3·992

gases by charcoal the results obtained by Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385) for the surface tensions of aqueous solutions of certain fatty acids. Szyszkowski found that if σ_0 is the surface tension of pure water, and σ that of a solution of the fatty acid of concentration c, then

$$\sigma_0 - \sigma = \beta \log (c/\alpha + 1),$$

where α is a constant decreasing as the length of the carbon chain in the acid increases, and β is a constant characteristic of the solvent. Applying this to charcoal adsorption, Iljin puts $\sigma_0 - \sigma = Q/S$, where S is the area of the adsorbing surface of the charcoal, the heat of adsorption thus being taken as a measure of the free energy of adsorption; c must be replaced by p, so that $Q = \beta S \log (p/\alpha + 1)$, which is more convenient for plotting if written as $Q = B \log (p + \alpha) - B \log \alpha$, where $B = \beta S$. Then, if Iljin's equation holds, the graph of $\log (p + \alpha)$ against Q should give a straight line intercepting the $\log (p + \alpha)$ axis at $\log \alpha$. The correct value of α is obtained by plotting with successive values of α, differing by small increments, until two consecutive values are reached such that one

gives a curve convex to one axis, and the next a curve convex to the other axis; the required value of α is then taken as the mean of these two values. Plotting the present results in this way, it was found that the best straight line was one that did not in general intercept the log $(p + \alpha)$ axis at log α (see, *e.g.*, Fig. 6), so that the results only fit a modified Iljin equation of the form $Q = B \log (p/\alpha + 1) + A$, where A is usually a positive quantity, but is occasionally negative. The results for sulphur dioxide do not agree with the equation at all, for even with $\alpha = 0$ (its minimal value, since it is essentially positive), a curved line is still obtained; this is true also of Titoff's results for ammonia (*Z. physikal. Chem.*, 1910, **74**, 641) which Iljin quotes as fitting his equation.

TABLE IV.

Values of α and B from Iljin's equation.

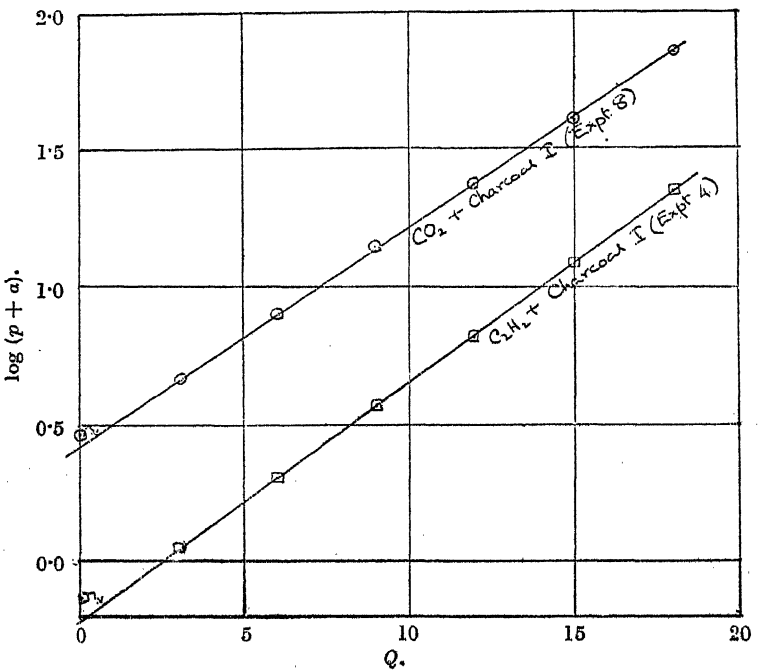
Gas.	Observer.*	a_Q. (cm. of Hg)	a_x.	$a \times 10^5$.	$b \times 10^6$.	B_Q (calc.).
At 0°.						
A	H.	—	60	259	1361	—
N_2	T., Expt. IX	55	—	270	1748	6·5
	T., Expt. X	55	—	,,	,,	7·35
	G., Char. I	—	50	,,	,,	—
	G., Char. II	50	55	,,	,,	5·98
	G., Char. III	—	50	,,	,,	—
	H.	—	50	,,	,,	—
CO	H.	—	50	285	1727	—
	G.	—	55	,,	,,	—
CH_4	H.	—	15	366	1591	—
CO_2	T.	2·80	2·80	701	1862	13·2
	R.	—	0·80	,,	,,	—
	G.	2·95	2·95	,,	,,	12·4
C_2H_2	G.	0·75	0·75	875	2293	11·3
C_2H_4	G., Expt. 9	0·20	—	889	2534	6·63
	G., Expt. 9*a*	0·20	0·20	,,	,,	6·28
C_3H_8	G.	0·16	0·16	1060	2800	11·6
N_2O	G., Char. I	1·65	1·70	728	1899	10·7
	G., Char. II	1·50	1·70	,,	,,	13·2
	G., Char. III	—	1·70	,,	,,	—
At 40·35°.						
N_2O	G., Char. I	10·0	12·0	728	1899	14·4
Adsorption by silica gel at 0°.						
N_2O	P.	—	35	728	1899	—

* H = Homfray; T = Titoff; G = Gregg; R = Richardson; P = Patrick (*J. Physical Chem.*, 1925, **29**, 421).

The value of α at a given temperature is roughly characteristic of a gas, varying considerably from one to another. This makes it possible to deduce the approximate value of α even when no heat measurements are available. For since $Q = kx^n$, we may put $kx^n = B \log (p + \alpha) - B \log \alpha$; and since n is never far from unity, the graph of log $(p + \alpha)$ against x also gives a nearly straight line; or, alternatively, the values of α necessary to give a straight

line with the measurements of Q and x, respectively, are quite close to one another, as shown by the figures for α derived by the two methods (Table IV). In this table, the gases are arranged in order of decreasing α, and it will be seen that they then stand in order of increasing a and b (the van der Waals constants), so that a complete parallelism exists between α, on the one hand, and a and b, on the other. (In the table, the suffix indicates whether the value is derived from the Q- or x-curve.) Moreover, the fact that the value of α decreases as the value of b (which is a measure of the size of the

FIG. 6.



molecule) increases, is analogous to Szyszkowski's result for the surface tension of solutions, in which he found that α decreases with increasing length of the hydrocarbon chain. This indicates that there is a close analogy between adsorption at a charcoal–gas interface and that at a water–gas interface, but it is difficult to pursue the analogy further.

Unfortunately, it is impossible to calculate B except by using heat measurements, for the equation $kx^n = B \log (p/\alpha + 1) + A$ shows that a knowledge of k is necessary for obtaining B. It will be seen that, in contrast to Szyszkowski's results, B does not remain constant for a given charcoal, though its variation is much less than

that of α. The non-constancy is possibly due to the fact that Q is not a true measure of the free-energy change; furthermore, the true analogue to Szyszkowski's β is not B, but B/S, and the adsorbing surface S of the charcoal may vary in an unknown way from gas to gas.

It is hoped to discuss more fully elsewhere some of the current theories of adsorption in the light of both the present results and those of other workers.

Summary.

1. Measurements are described of the heat of adsorption, the equilibrium pressure, and the amount adsorbed, for eight gases on a standard charcoal at 0°, with the aid of Bunsen's ice calorimeter. A few experiments were also carried out at 40·35° using a phenol calorimeter, and in some cases the charcoal was replaced by other standard samples.

2. The phenomenon of hysteresis has been traced to the presence of some non-condensable gas in the adsorption system, as other workers have found.

3. For the integral heat of adsorption Q, the relationship $Q = kx^n$ has been found to hold, where x is the amount adsorbed and k and n are constants; n is roughly characteristic of the gas and lies between approximately 0·9 and 1·0; k is slightly decreased by previous adsorption and subsequent elimination of the same or another gas.

4. The Williams–Henry equation, $\log x/p = A_0 - A_1x$, where p is the equilibrium pressure and A_0 and A_1 are constants at constant temperature, is fairly satisfactory for all except the readily condensable gases.

5. With similar limitations, the relationship between p and Q is expressed fairly well by a modified Iljin equation of the form $Q = B \log (p/\alpha + 1) + A$. A close parallelism exists between the value of α and the corresponding values of the constants a and b in van der Waals's equation, a fact which recalls the results of Szyszkowski for the surface tension of aqueous solutions.

In conclusion, the author desires to thank Professor J. C. Philip, F.R.S., for his kindly help and advice during the whole of this work; and also the Department of Scientific and Industrial Research for a grant which enabled him, as student-in-training, to carry out the experimental part of this work at the Imperial College of Science and Technology.

UNIVERSITY OF LONDON,
KING'S COLLEGE, W.C. 2.

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CCI.—*The Constitution of the Disaccharides. Part XIII. The γ-Fructose Residue in Sucrose.*

By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and VINCENT STANLEY NICHOLSON.

THE γ-fructose residue in sucrose was isolated by one of us in the form of tetramethyl γ-fructose (Haworth, J., 1915, **107**, 12; 1920, **117**, 199). This unstable sugar was characterised by its dextrorotation and by the ease with which it decolorised aqueous permanganate, but further study has revealed a remarkable and unexpected behaviour. In contact with dilute hydrochloric acid at 80°, or on digestion with acetic anhydride in presence of sodium acetate, this methylated ketose undergoes changes involving loss of three of its methoxyl groups as methyl alcohol. This circumstance explains many of the discordant results quoted in the literature of this sugar, and serves also to emphasise the danger attaching to the acceptance of preconceived ideas of the properties of methylated sugars.

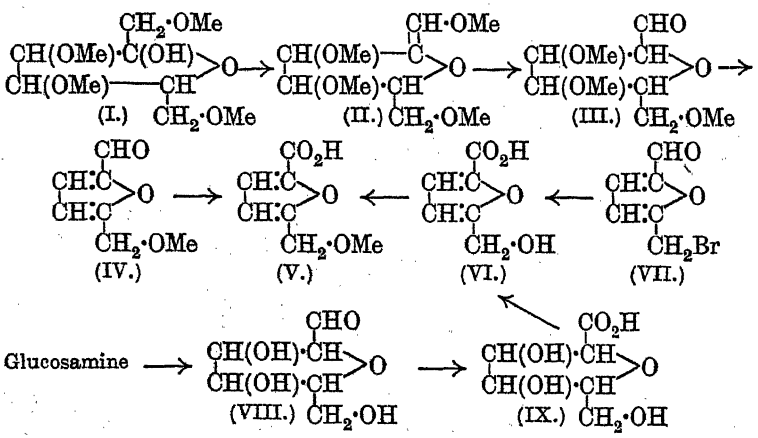
When 8% hydrochloric acid was used, more than a third of the product was collected as a typical aldehyde, having an odour like that of benzaldehyde and distilling at about 54°/0·07 mm. It was optically inactive, restored the colour to Schiff's reagent, reduced Fehling's solution, and decolorised permanganate instantly. The aldehyde was characterised by its giving crystalline derivatives; an *oxime*, m. p. 103—104°, and a *semicarbazone*, m. p. 166—167°. Its molecular composition, $C_7H_8O_3$, was recognised by this means, and its general properties suggested its relationship to furan.

The action of hot mineral acid on free sugars containing exposed hydroxyl groups, *e.g.* the pentoses, was already recognised as involving condensation with elimination of water, leading to the formation of furfural or similar products; but in the special case now under review, the hydroxyl positions in fructose are methylated, leaving only the reducing group exposed.

In a previous paper (Haworth and Hirst, J., 1926, 1858), reference was made to the tendency of tetramethyl γ-fructose to pass into furan derivatives during oxidative degradation, and it was there suggested that many of the anomalies attending the constitutional study of this sugar might be attributed to this behaviour. The present results extend and confirm this observation. It was also indicated that an explanation of this behaviour was to regard tetramethyl γ-fructose as a substituted hydrofuran (I), and this provisional formula is strongly supported by the series of transformations which are now recorded.

It is necessary to proceed with caution in the structural interpretation of these observations, and we have relied essentially on the isolation of crystalline products which in the last resort have been compared with substances of known constitution described in the literature. Evidence of the identity of the final products obtained by the conversion of tetramethyl γ-fructose into furan derivatives by contact with hydrochloric acid is now furnished.

The aldehyde, originating as already described, was identified as *ω-methoxy-5-methylfurfural* (IV), since it gave on oxidation with permanganate (compare Frankland and Aston, J., 1901, **79**, 515) *ω-methoxy-5-methylfuran-2-carboxylic acid* (V), m. p. 72—73°, the constitution of which was confirmed by comparison with the crystalline acid isolated from two known sources: ω-bromo-5-methylfurfural (VII) (Fenton and Gostling, J., 1899, **75**, 429) gave on hydrolysis and oxidation *ω-hydroxy-5-methylfuran-2-carboxylic acid* (VI), m. p. 165—167°, the constitution of which had been previously determined by conversion of the crystalline bromide into furan-2 : 5-dicarboxylic acid (dehydromucic acid), identical with that obtained from mucic acid (Hill and Jennings, *Amer. Chem. J.*, 1893, **15**, 159; Hill and Sawyer, *ibid.*, 1898, **20**, 169). When the ω-hydroxy-5-methylfuran-2-carboxylic acid (VI) isolated by these methods was methylated with methyl iodide and silver oxide, we obtained an ester which on hydrolysis gave the crystalline ω-methoxy-5-methylfuran-2-carboxylic acid (V), m. p. 72—73°, identical with that which we had isolated as a transformation product of tetramethyl γ-fructose.



No simple explanation suffices to interpret the transformation of tetramethyl γ-fructose to this furan derivative. On the hypothesis that this sugar contains already a substituted hydrofuran ring (I),

a reasonable explanation of the series of conversions is given in the formulæ above. On this interpretation, the first stage of the transformation from tetramethyl γ-fructose (I) to ω-methoxymethylfurfural (IV) is the elimination of water by removal of the reducing hydroxyl group along with hydrogen of the methylated primary alcohol residue in the first terminal position. This would give the compound (II), containing a methoxymethylene residue which, hydrolysing with ease to the hydroxymethylene group, thereafter functions as an acidic residue, the compound now being an enolic form of the aldehyde (III), and there can be little doubt that the introduction of an aldehyde group follows a course similar to that which is here represented. It may be that the compound (III) is readily formed from tetramethyl γ-fructose and may frequently be present in this sugar as an impurity. It is indeed a variety of trimethyl chitose, and the realisation of this has led us to investigate the transformation of glucosamine into chitose by the methods described by Fischer. This further extension of our work has readily afforded us an alternative means of identifying our products (IV) and (V).

Thus, it has already been shown by Fischer that glucosamine is converted by nitrous acid into chitose (VIII), and that the latter on oxidation with bromine passes into chitonic acid (IX). During acetylation in the presence of acetic anhydride and sodium acetate, chitonic acid lost two molecules of water and passed into ω-acetoxy-5-methylfuran-2-carboxylic acid, which on hydrolysis gave ω-hydroxy-5-methylfuran-2-carboxylic acid (VI). We have confirmed this series of transformations leading from glucosamine, and the final product (VI) was identical with the compound we had obtained as described above by interconversion from (VII). Finally, the specimen of hydroxymethylfurancarboxylic acid obtained from glucosamine gave on methylation ω-methoxy-5-methylfuran-2-carboxylic acid (V) identical with that obtained from tetramethyl γ-fructose.

Thus a cycle of inter-relationships has been established between γ-fructose derivatives on the one hand and glucosamine, chitose, and chitonic acid on the other. The allocation of the butylene oxide formula (I) to tetramethyl γ-fructose, representing this sugar as a substituted hydrofuran, therefore receives the same experimental sanction as the formulæ ascribed by Fischer (Fischer and Tiemann, *Ber.*, 1894, **27**, 138; Fischer and Andreae, *Ber.*, 1903, **36**, 2587) to chitose and to chitonic and chitaric acids. The results now indicated afford definite proof of the presence in tetramethyl γ-fructose of two terminal methoxy-groups, $-CH_2 \cdot OMe$. These serve to distinguish the structural representation of this sugar from

the amylene oxide type which is normal crystalline tetramethyl fructose (Haworth and Hirst, *loc. cit.*).

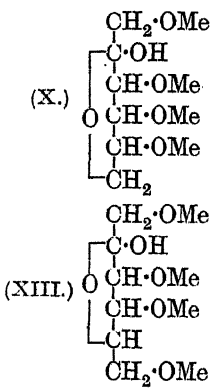
There now remains to be considered the evidence arising from the oxidation of tetramethyl γ-fructose (*a*) with nitric acid and (*b*) with permanganate. The latter degradation will be dealt with in a later paper, but we have again investigated the nitric acid method of oxidation employed by Haworth and Linnell (J., 1923, **123**, 294), and have conducted this work alongside a similar investigation on the normal crystalline tetramethyl fructose.

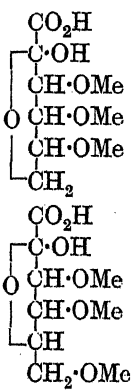
Previous knowledge of the behaviour of nitric acid towards aldoses had established a predilection in favour of the view that the reducing group of sugars was the first to suffer attack in the presence of such an oxidising medium. That such is not the case, however, with ketoses has been made abundantly clear by Haworth, Hirst, and Learner (this vol., p. 1040). It was, for example, shown that the first product of oxidation of normal crystalline tetramethyl fructose (X) was a trimethoxy-lactol acid (XI), giving a crystalline ethyl ester (XII) and a crystalline methyl ester; and the latter gives a higher methylated homologue (crystalline), which is converted into a crystalline amide by the agency of ammonia.

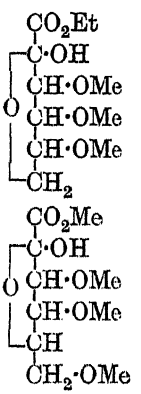
With the insight and experience gained by investigation of this simpler example of the oxidation of a fructose derivative, we have now applied similar methods to the examination of the initial oxidation product of tetramethyl γ-fructose obtained by Haworth and Linnell by the use of dilute nitric acid. These authors recorded the isolation of an oxidation product giving the analysis: C, 50·5; H, 7·3; OR (calc. as OMe), 47·3%. This product was considered to be, on the basis of its analytical data and its general behaviour, a trimethoxy-δ-valerolactone, $C_8H_{14}O_5$ (Calc.: C, 50·5; H, 7·4; OMe, 48·9%). We have since isolated this product many times and in yields representing more than 70% of the tetramethyl γ-fructose employed and have confirmed these analytical figures repeatedly.

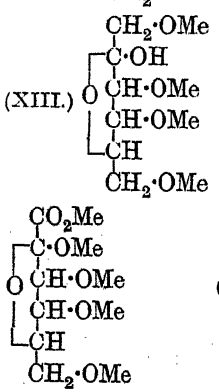
In view, however, of the exceptional behaviour of tetramethyl γ-fructose towards dilute mineral acids, it seemed to us reasonable to suspect that, although the same oxidation product appeared to be constantly formed, the analytical data might be influenced by the presence of traces of the transformation product (III), (IV), or (V), arising in the way we have demonstrated in the earlier part of this paper. If so, it appeared to us that Haworth and Linnell's oxidation product might be analogous in composition and structure to the initial product of oxidation of normal tetramethyl fructose, that is, that the supposed lactone $C_8H_{14}O_5$ might be the ethyl ester of a trimethoxy-lactol acid, $C_{11}H_{20}O_7$ (XVII), isomeric with (XII),

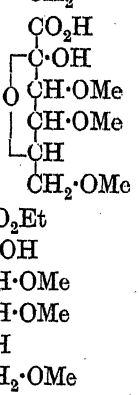
for which the calculated figures are: C, 50·0; H, 7·6; OR (as OMe), 47·0%. This has indeed proved to be the case. The product, resembling a lactone in many of its properties, is unstable to alkali through retaining the free reducing group of the original sugar, and the titration data are for this reason slightly higher than those required for the lactol ester $C_{11}H_{20}O_7$, and may readily be interpreted to satisfy the lactone formula $C_8H_{14}O_5$. We have isolated the corresponding methyl ester (XV) in yields of 75%, but in this case also the carbon value is slightly high owing to the presence of furan derivatives or their intermediate compounds as impurity. That this substance is not a lactone is, however, shown by its conversion into the higher homologue (XVI) of the lactol methyl ester by further methylation. This product no longer reduced Fehling's solution, was comparatively stable towards alkali, and gave a titration value approximating closely to that required by this constitution. Treatment of this methylated product with methyl-alcoholic ammonia gave a crystalline amide (XVIII), m. p. 100—101°, the complete analysis of which established the molecular weight of the original ester, identifying it as being structurally analogous to the product of oxidation obtained under similar conditions from normal crystalline tetramethyl fructose.

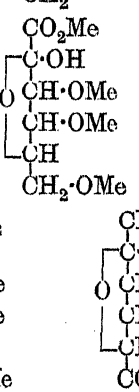

(X.)

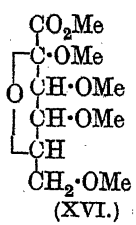

(XI.)

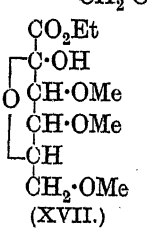

(XII.)

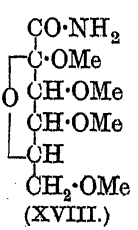

(XIII.)

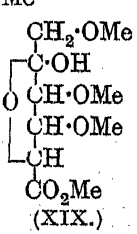

(XIV.)


(XV.)


(XVI.)


(XVII.)


(XVIII.)


(XIX.)

The possibility has not escaped us that the methyl ester, $C_{10}H_{18}O_7$, might also be formulated as in (XIX), representing the carboxyl

group in position 6 instead of in position 1 as given in formula (XV), but there are many indications which favour the latter structure. In the first place, the oxidations of both the normal and the γ-form of tetramethyl fructose proceeded on exactly parallel lines and led to analogous products. The oxidation of the normal sugar is definitely shown not to affect position 6 (Haworth, Hirst, and Learner, *loc. cit.*). Again, the action of hydrochloric acid on tetramethyl γ-fructose has in the present paper been shown to lead readily to an attack on the $-CH_2 \cdot OMe$ group in position 1. In both cases the vulnerable position towards the action of nitric acid may be expected to be that of the group in position 1. The further oxidation of these products will form the subject of a future communication.

It seems probable that oxidation products similar to the above lactol esters have also been isolated by other workers in the course of investigations on derivatives of γ-fructose, *e.g.*, in the oxidation of tetramethyl γ-fructose with nitric acid as conducted by McOwan (J., 1926, 1737). This author allocated formulæ based on the analytical data given by liquid specimens which were probably not homogeneous. Doubtless the compound represented by (XV) was also obtained by the above author, who assigned to it the formula of a keto-ester containing a four-carbon chain, one of the alternatives suggested being that of a substituted acetoacetic ester.

The present constitutional position in regard to tetramethyl γ-fructose is that, as we have shown in the earlier part of this paper, this sugar cannot contain an amylene oxide ring, since there is present a $-CH_2 \cdot OMe$ group in each of the terminal positions. The remaining possibilities are that the oxide ring is butylene-, propylene-, or ethylene-oxidic, but the 2 : 3-oxide ring is excluded inasmuch as 3-methyl fructose gives rise to a γ-methylfructoside (Allpress, J., 1926, 1720), and the 1' : 2-oxide is excluded by the above results. We definitely favour the allocation of a butylene oxide formula, since this affords the simplest explanation of the peculiar transformations which tetramethyl γ-fructose undergoes, leading with the greatest facility to furan compounds, and secondly, because in the series of aldoses the γ-sugars which have been studied are butylene oxidic.

EXPERIMENTAL.

For the sake of brevity, numerous preliminary experiments are given in condensed form as follows:

Purity of Tetramethyl γ-Fructose.—Tetramethyl γ-fructose is acted upon both by acids and by alkalis, and in order to obtain a pure specimen, prolonged contact of the sugar even with dilute acid, especially at high temperatures, must be avoided. If suitable

precautions are not observed, the first distillation product may contain sufficient aldehydic material to give a pronounced colour to Schiff's reagent. Careful hydrolysis of heptamethyl sucrose (Haworth, J., 1915, **107**, 12; 1920, **117**, 199), the most convenient source, with 0·4% aqueous hydrochloric acid at 60° as originally recommended, followed by neutralisation of the acid with barium carbonate and extraction of the tetramethyl sugar with chloroform, yielded a product the physical constants of which were in agreement both with those previously recorded and with those of a specimen of tetramethyl γ-fructose which had been subjected to further rigorous purification. This was effected by means of bromine, which does not attack tetramethyl γ-fructose, but oxidises a methylated aldose (Haworth and Mitchell, *loc. cit.*). Tetramethyl γ-fructose in 20% aqueous solution was treated with half its weight of bromine for 16 hours at 35°. After removal of the bromine by aeration in the cold, the solution was neutralised with barium carbonate and the purified tetramethyl γ-fructose was extracted by chloroform and distilled. The final product was neutral to litmus, gave no colour with aniline acetate or Schiff's reagent, and had $[\alpha]_D^{16^\circ} + 31{\cdot}3^\circ$ ($c = 2{\cdot}015$) and $n_D^{13^\circ}$ 1·4513.

With regard to the method of purification recommended by McOwan (*loc. cit.*), who employed alkaline hypoiodite, it was found that the action of very dilute alkali ($N/30$) on tetramethyl γ-fructose resulted in changes such that the solution very quickly contained material which gave a positive test with Schiff's reagent. Further details of these experiments will be communicated shortly, but in the meantime the results are sufficiently striking to warrant the opinion that the use of alkali at any stage of the purification of the sugar should be avoided. Even with neutral hypoiodite the purest samples of tetramethyl γ-fructose give a figure corresponding to a content of 2·8% of tetramethyl glucose. Incidentally, it was found to be undesirable to use octamethyl sucrose as a source of tetramethyl γ-fructose, inasmuch as a specimen, obtained in this way, which had not been subjected to the bromine treatment gave on oxidation with nitric acid small quantities of *d*-dimethoxysuccinic acid and *i*-xylotrimethoxyglutaric acid, both of which were recognised as their crystalline diamides (for method of isolation, see Hirst, J., 1926, 350).

Oxidation of Tetramethyl γ-Fructose with Nitric Acid.—A series of oxidations was carried out with both concentrated (*d* 1·42) and dilute (*d* 1·2) nitric acid under various conditions of temperature and times of oxidation, the products being isolated both as esters (methyl and ethyl) and also by simple distillation without the use of alcohol at any stage of the experiment. Details of the methods

employed are given in earlier communications (Haworth and Hirst, *loc. cit.*) and it will be sufficient to give here a summary of the results.

I. *With nitric acid, d* 1·2. (Time, 20 hours at 60° or 9 hours at 90°.)

When the oxidation product was collected as an acid, *contact with alcohol being avoided*, distillation gave a strongly reducing syrup which was evidently a complex mixture of products. From this, crystals of the optically inactive acid $C_8H_{10}O_5$ (m. p. 88—89°; Haworth and Hirst, J., 1926, 1858) separated on standing. Fractionation of the remaining syrup failed to give any homogeneous material, and the colourless distillate, in addition to reducing Fehling's solution, was unstable when kept and became nearly black in the course of a few weeks.

When methyl alcohol was used for esterification, the distilled product invariably gave the strongly reducing methyl ester, $C_{10}H_{18}O_7$, of the acid the ethyl ester of which was obtained under different conditions of working by Haworth and Linnell (*loc. cit.*). The prolonged treatment with nitric acid required in this experiment led to the formation of a considerable quantity of oxalic acid.

II. *With nitric acid, d* 1·42. By the use of the stronger acid, the time required for the oxidation was curtailed, much of the decomposition caused by long contact with an acid medium thus being obviated. Isolation of the product as methyl ester now gave in larger yield (up to 75% of the weight of the sugar used) a methyl ester, the physical properties of which approximated to $n_D^{15°}$ 1·4500; $[\alpha]_D$ + 30° in water, and gave analytical figures in fairly close agreement with those required by a compound of formula $C_{10}H_{18}O_7$ (Found: C, 48·4; H, 7·6; OMe, 49·6. Calc.: C, 48·0; H, 7·2; OMe, 49·6%). Under similar conditions of oxidation but with the use of ethyl alcohol for esterification, equivalent yields of the substance described by Haworth and Linnell were obtained. The analytical figures formerly given were confirmed and found to correspond with those required by a substance of formula $C_{11}H_{20}O_7$.

The methyl ester was unstable to alkali and vigorously reduced Fehling's solution, accurate titration figures being therefore impossible to obtain. It was unstable even on being kept at the ordinary temperature in a desiccator, showed a progressive increase in the value of n_D amounting to + 0·004 approximately after 3 weeks, and became distinctly darker in colour.

Methylation of the Product $C_{10}H_{18}O_7$.—With the view of determining the nature of the reducing group present, the strongly reducing methyl ester $C_{10}H_{18}O_7$ was methylated with Purdie's reagents. The product on distillation gave a main fraction distilling at a bath

temperature of 165°/16 mm.; $n_D^{20°}$ 1·4392; $[\alpha]_D$ + 9° in methyl alcohol (Found: C, 49·9; H, 7·8; OMe, 57·0; CO_2Me, 24·0. $C_{11}H_{20}O_7$ requires C, 50·0; H, 7·6; OMe, 58·7; CO_2Me, 22·4%). It was now non-reducing. Amide formation was effected by dissolving the ester in methyl alcohol saturated with ammonia. No deposition of crystals occurred until the solvent had been evaporated; the residual syrup then crystallised. The long needles so obtained were drained on porous earthenware and washed with ether and light petroleum; they then melted at 95—100°.

Preparation of the Amide $C_{10}H_{19}O_6N$, m. p. 100—101°.—The results described up to this point were regarded as merely preliminary in view of the uncertainty attaching to any interpretation based solely on the examination of liquid substances. It had become apparent during the course of the experiments that the action of acid on the strongly reducing oxidation products, unless carefully controlled, led to profound and complex changes even during the processes necessary for the isolation and characterisation of the substances in question. Accordingly, another series of experiments was carried out in which the contact with acid was reduced to the minimum and the sensitive reducing group was protected as soon as possible by methylation. In this way substantial yields of the above-mentioned crystalline amide (m. p. 95—100°) were obtained, amounting to 40% by weight of the tetramethyl γ-fructose used.

Ten g. of tetramethyl γ-fructose were treated with 70 c.c. of nitric acid (*d* 1·420). Vigorous oxidation began at 70°; the temperature was thereafter gradually raised in the course of an hour to 92° and maintained for 1¾ hours. The nitric acid was then removed in the usual way at 50°/15 mm., the distillation with repeated addition of water being carried on for 5 hours only. Methyl alcohol was added, and distilled off to remove water, and the residual syrup was boiled for 4 hours with 70 c.c. of methyl alcohol. Removal of the solvent yielded a syrup which still contained a little nitric acid but was soluble in methyl iodide. The solution in methyl iodide was neutralised with silver oxide (3 g.), and methylation with silver oxide (30 g.) then proceeded under the usual conditions, the reaction being sufficiently vigorous in the cold to cause the solvent to boil. The product was purified by distillation, giving (*a*) 1·2 g., mainly methyl oxalate and solvent; (*b*) 4·4 g., bath temp. 161°/16 mm., $n_D^{15°}$ 1·4422; (*c*) 3·0 g., bath temp. 166°/16 mm., $n_D^{15°}$ 1·4442; and (*d*) 1·1 g., bath temp. 180°/16 mm., $n_D^{15°}$ 1·4470. There was no sign of decomposition at any stage of the distillation. Fractions (*b*) and (*c*) appeared to be essentially the same product or mixture of products.

Fraction (*b*) was a colourless, mobile syrup without action on Fehling's solution and was not decomposed to give coloured substances by hot alkali; $[\alpha]_D$ — 8° in methyl alcohol ($c = 2{\cdot}452$) (Found: C, 49·0; H, 7·5; OMe, 57·0; CO_2Me, 32·0%). The analytical figures revealed that the distillate was not a single substance, but amide formation proved that it consisted very largely of the methyl ester (methylated), $C_{11}H_{20}O_7$. A solution of 1·3 g. in 10 c.c. of methyl alcohol saturated with ammonia deposited no crystalline material after being kept for a week. The clear solution was then allowed to evaporate, whereupon the resulting syrup crystallised. The crystals were extracted with boiling light petroleum (b. p. 60—80°) and could easily be recrystallised from this solvent. The yield of pure recrystallised material was 0·5 g. In all, from 6·3 g. of fractions (*b*) and (*c*), 3·0 g. of pure recrystallised *amide* were obtained. It crystallised from light petroleum in tufts of interlacing needles resembling cotton-wool in appearance. It was very soluble in methyl and ethyl alcohols and water, less soluble in acetone, and slightly soluble in ether. M. p. 100—101°; $[\alpha]_D$ —76° in water ($c = 1{\cdot}099$) (Found: C, 48·0; H, 7·8; N, 5·4; N, by titration, 5·5; OMe, 47·7. $C_{10}H_{19}O_6N$ requires C, 48·2; H, 7·6; N, 5·6; OMe, 49·8%).

The residue, after extraction with light petroleum, contained some solid matter embedded in a stiff gum. The syrup was removed by extraction with benzene, and the powdery residue was recrystallised from alcohol containing light petroleum. M. p. 177—178°. This material was insoluble in the usual organic solvents except ethyl and methyl alcohols. It was readily soluble in water. Apparently it was not a pure substance, but the analytical figures indicated clearly that it represented the amide of that portion of the original oxidation product which was responsible for the low value of carbon and the high value of CO_2Me. Yield, 0·6 g. from 6 g. of ester (Found: C, 40·3; H, 6·2; N, 12·2; OMe, 39·1%).

The Action of Acetic Anhydride and Sodium Acetate on Tetramethyl γ-Fructose.—Tetramethyl γ-fructose (5 g.), anhydrous sodium acetate (5 g.), and acetic anhydride (50 g.) were heated together at 120° for 1½ hours and then at the boiling point of the mixture for another hour. The solution was then poured into water (4 vols.), and after a few hours the product was extracted with chloroform. Removal of the solvent left a syrup containing acetic acid, which was removed by keeping the mixture in a desiccator over potassium hydroxide. Distillation now gave a series of fractions with a wide range of boiling points and refractive indices, revealing the presence of a complex mixture of substances, the lowest-boiling fraction of which represented the most homogeneous portion. This (0·7 g.;

b. p. about 55°/0·01 mm.; $n_D^{13^\circ}$ 1·4985) was a colourless oil which darkened when kept and gave all the reactions of an unstable aldehyde. It had the odour of furfural, readily combined with phenylhydrazine to give a liquid phenylhydrazide, reduced Fehling's solution, gave Schiff's test for aldehydes, and produced an intense red colour with aniline acetate. It showed slight acidity towards litmus, but this was probably due to the presence of impurities. Analysis showed that the product was not a single substance (Found: C, 57·4; H, 6·6; OMe, 31·7%), but it was proved to be largely ω-methoxy-5-methylfurfural by the following series of reactions. Treated with semicarbazide hydrochloride and sodium acetate, a concentrated aqueous solution of the aldehyde immediately gave a precipitate of the crystalline semicarbazone, m. p. 166—167° after recrystallisation from alcohol. Similar treatment with hydroxylamine hydrochloride and sodium acetate gave the oxime as a mobile oil which readily crystallised. Recrystallised from light petroleum (b. p. 40—60°) containing a little ether, it was obtained in colourless, matted needles, m. p. 103—104°. Further details and analytical figures for these compounds are given in the following paragraph.

The Action of Hydrochloric Acid on Tetramethyl γ-Fructose. Preparation of ω-Methoxy-5-methylfurfural.—ω-Methoxymethylfurfural was more readily obtainable by the action of hydrochloric acid on tetramethyl γ-fructose. Tetramethyl γ-fructose was mixed with twice its weight of 8% hydrochloric acid and heated at 80°. The solution darkened and methyl alcohol distilled over, this being identified by the usual tests. After treatment in this way for 1½ hours, the solution was cooled and repeatedly extracted with chloroform. The extracts were neutralised with sodium carbonate, dried, and filtered. After removal of chloroform, a mobile syrup remained (70%), which was divided into two fractions by distillation: I, b. p. about 54°/0·07 mm., n_D 1·4908 (yield over 30%); II, b. p. up to 82°/0·04 mm., n_D 1·4597. Fraction I had a powerful aldehydic odour, restored the colour to Schiff's reagent, gave a red coloration with aniline acetate, and immediately decolorised neutral permanganate.

The *semicarbazone* was prepared and twice recrystallised from alcohol; it melted at 166—167° and was identical with that obtained by the action of acetic anhydride and sodium acetate on tetramethyl γ-fructose (Found: C, 48·7; H, 5·5; OMe, 15·4; N, 21·7. $C_8H_{11}O_3N_3$ requires C, 48·7; H, 5·6; OMe, 15·7; N, 21·3%). The *oxime* also was prepared; after recrystallisation from light petroleum and ether, it melted at 103—104° and was identical with that obtained and described in the previous section (Found:

C, 54·1; H, 5·9; N, 9·1; OMe, 18·8. $C_7H_9O_3N$ requires C, 54·2; H, 5·8; N, 9·05; OMe, 20·0%).

Fraction II contained some of the aldehyde already examined, and probably some unchanged tetramethyl γ-fructose and intermediate products.

In order to study the effect of more drastic treatment with mineral acid, the following experiment was carried out: The sugar (10 g.) was treated with concentrated hydrochloric acid (4 c.c.), the temperature being very gradually raised until at 80° a liquid began to distil. This was methyl alcohol. After remaining over-night at room temperature, the mixture was heated at 50°/0·1 mm. until the methyl alcohol and water had been removed, leaving a residue (6 g.). The bath temperature was then raised and, the first two drops being rejected, a fraction (4·4 g.) was obtained, b. p. 70—75°/0·4 mm., $n_D^{15°}$ 1·5060. A small, dark residue remained.

Refractionation of 3 g. of the above material gave (1) 0·3 g., b. p. below 50°/0·05 mm., $n_D^{15°}$ 1·5020; (2) 1·7 g., b. p. 53°/0·05 mm., $n_D^{15°}$ 1·5105; (3) 0·9 g., b. p. above 55°/0·05 mm., $n_D^{15°}$ 1·5078. The middle fraction was crude *ω-methoxy-5-methylfurfural* (Found: C, 58·3; H, 6·0; OMe, 24·1. $C_7H_8O_3$ requires C, 60·0; H, 5·7; OMe, 22·1%). The oxime (m. p. 103—104°) and the semicarbazone (m. p. 166—167°) were prepared by the methods given above and were identical with the corresponding derivatives of the aldehyde prepared by the action of acetic anhydride on tetramethyl γ-fructose. Mixed melting-point determinations of the corresponding oximes and semicarbazones gave no depression, the values being 103—104° and 166—167° respectively.

The analytical figures given by the aldehyde indicated that a small quantity of a more highly methylated substance was present, and attempts were made to obtain the pure aldehyde by regenerating it from the crystalline semicarbazone. Hydrolysis by dilute hydrochloric acid or by oxalic acid failed to give satisfactory results. The use of 18% hydrochloric acid appeared to liberate the aldehyde, but it changed at once to a dark, viscid mass which still retained the characteristic odour of the aldehyde.

Oxidation of ω-Methoxy-5-methylfurfural to give ω-Methoxy-5-methylfuran-2-carboxylic Acid.—The oxidation was carried out by Frankland and Aston's method (J., 1901, **79**, 515). Calcium hydroxide (1·5 g.) was made into a paste with water (5 c.c.), and the aldehyde (1 g.) was added; 13·6 c.c. of a solution of potassium permanganate containing 5·5 g. per 100 c.c. were then added, with constant stirring, during 30 minutes, the temperature being maintained throughout at 10° by addition of ice as required. The mixture was heated on the steam-bath and filtered hot, and the

precipitated manganese oxides were repeatedly washed with hot water. The united filtrates were evaporated to dryness under diminished pressure, and the acidified residue extracted with dry ether. The extract yielded a dark syrup, which was dissolved in a little water and carefully neutralised with dilute sodium hydroxide solution. Evaporation under diminished pressure gave the sodium salt, which, after being freed from some syrupy material by washing with ether, was clean and hard. A solution of it in a very slight deficiency of dilute hydrochloric acid was evaporated to dryness under diminished pressure, and the free organic acid extracted by dry ether. Removal of the ether gave a mobile syrup which crystallised when stirred. The solid was drained on porous earthenware and the pure *ω-methoxy-5-methylfuran-2-carboxylic acid* was obtained by recrystallisation from light petroleum; it melted at 72—73° after slight softening at 69° and was optically inactive (Found: C, 54·0; H, 5·1; OMe, 18·9. $C_7H_8O_4$ requires C, 53·9; H, 5·1; OMe, 19·9%. 0·1996 G. required 12·7 c.c. of *N*/10-NaOH for neutralisation. Calc. for $C_7H_8O_4$, 12·8 c.c.).

Preparation of ω-Methoxy-5-methylfuran-2-carboxylic Acid from ω-Bromo-5-methylfurfural.—The ω-bromomethylfurfural was prepared by Fenton and Gostling's method (J., 1899, **75**, 429), the following modification giving an improved yield. Fructose (15 g.) was covered with dry chloroform (250 c.c.) saturated with hydrogen bromide. The mixture was heated at 60—65° for one hour and then kept at room temperature over-night. The product (4·9 g.), after recrystallisation from ether, had m. p. 60—61°. The pure crystalline ω-bromomethylfurfural (7 g.) was simultaneously hydrolysed and oxidised by means of silver oxide (60 g.) suspended in boiling water (Fenton and Gostling, *loc. cit.*). Isolation of the ω-hydroxymethylfurancarboxylic acid yielded a light brown, crystalline solid as crude product (5·6 g.), recrystallisation of which from ethyl acetate gave material having m. p. 159—161°; this m. p. was raised to 165·5—167° (turning brown at 158°) by two further crystallisations from alcohol–toluene. Fischer and Andreae give m. p. 165—167° (turning brown at 157°). (Found: C, 50·5; H, 4·3. Calc.: C, 50·7; H, 4·2%).

Methylation of ω-Hydroxy-5-methylfuran-2-carboxylic Acid.—The acid (1 g.) was heated at 45—50° with methyl iodide (20 g.) and silver oxide (10 g.), addition of methyl alcohol (4 c.c.) being necessary to effect solution of the acid. Isolation of the product was followed immediately by a second methylation under similar conditions, the addition of only 1 c.c. of methyl alcohol now being necessary. For the third methylation no methyl alcohol was required. The product, on distillation, gave *methyl ω-methoxy-*

5-*methylfuran*-2-*carboxylate* (0·8 g.) as a colourless liquid, b. p. about 61°/0·05 mm., $n_D^{19.5°}$ 1·4938 (Found: OMe, 35·3. $C_8H_{10}O_4$ requires OMe, 36·5%).

ω-*Methoxy*-5-*methylfuran*-2-*carboxylic Acid*.—The above ester (0·2 g.) was warmed on the water-bath for 2 hours with a 1% aqueous solution of sodium hydroxide (10 c.c.). Hydrochloric acid was then added until the solution was acid to Congo-paper, and the product was isolated by extraction with ether. Evaporation of the solvent gave a colourless syrup which immediately crystallised. Recrystallisation from light petroleum (b. p. 40—60°) gave pure ω-methoxymethylfurancarboxylic acid, which, alone or mixed with a specimen prepared from tetramethyl γ-fructose, melted at 72—74° after softening slightly at 69°.

Preparation of ω-*Methoxy*-5-*methylfuran*-2-*carboxylic Acid from Glucosamine*.—Glucosamine hydrochloride (10 g.) was treated with nitrous acid to give chitose, and the latter, without being isolated, was oxidised by bromine to chitonic acid. The calcium salt of this, after being recrystallised from water (yield, 3·3 g. Found: Ca, 9·35. Calc.: Ca, 9·3%), was converted (2·8 g.) into ω-acetoxymethylfurancarboxylic acid by the action of sodium acetate and acetic anhydride. The product (1·9 g.), recrystallised from ether, had m. p. 115—118° (Found: C, 52·0; H, 4·7. Calc. for $C_8H_8O_5$: C, 52·2; H, 4·4%).

The acetyl compound was hydrolysed by means of baryta, and the free acid obtained melted, alone or mixed with ω-hydroxymethylfurancarboxylic acid prepared from ω-bromomethylfurfural, at 165—167°, colouring slightly at about 156°. The hydroxy-acid (0·5 g.) was heated with methyl iodide (10 g.), silver oxide (5 g.), and methyl alcohol (2—3 c.c.) at 45—50°; the methyl ester thus obtained was hydrolysed by means of *N*/4-sodium hydroxide (30 c.c.) for 2 hours on the water-bath, and the solution of the sodium salt was acidified. The ω-methoxy-5-methylfuran-2-carboxylic acid, after recrystallisation from ether, melted at 72—73°, alone or mixed with the specimens prepared from tetramethyl γ-fructose and from ω-bromomethylfurfural.

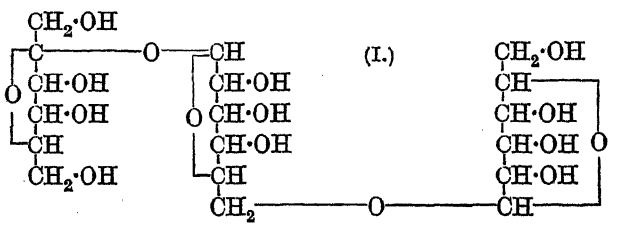
UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCII.—*The Constitution of the Disaccharides. Part XIV. Melibiose and its Relationship to Raffinose.*

By WILLIAM CHARLTON, WALTER NORMAN HAWORTH, and WILFRED JOHN HICKINBOTTOM.

RAFFINOSE was the subject of a constitutional study in an earlier communication (Haworth, Hirst, and Ruell, J., 1923, **123**, 3125), wherein it was stated that completely methylated raffinose gives rise on hydrolysis to three methylated fragments: (1) normal tetramethyl galactose; (2) 2 : 3 : 4-trimethyl glucose*; (3) tetramethyl γ-fructose, and in the course of recent work these experimental results were confirmed. The constitution advanced for this trisaccharide, translated into terms of the revised formulæ for the constituent hexoses (Charlton, Haworth, and Peat, J., 1926, 89; Haworth and Hirst, *ibid.*, p. 1858), is formulated



(I.)

It was also stated that "from this determination of the structure of raffinose it may be inferred that the constitution of melibiose proposed by Haworth and Leitch (J., 1919, **115**, 809) receives substantial confirmation, but inasmuch as structural changes may occur in the resulting disaccharide when the fructose residue is eliminated from raffinose, it has been thought desirable to undertake a separate investigation of melibiose, which is now in progress."

The results of that investigation are now presented, and they support the view that the glucose and galactose residues occurring in raffinose are identical with those in melibiose. During the isolation of hendecamethyl raffinose in the earlier work, a small quantity of a crystalline by-product was encountered, m. p. 78°, which was considered to be a completely methylated disaccharide, probably melibiose. This had been formed by partial hydrolysis of raffinose during the process of methylation. This crystalline substance when purified (m. p. 101—103°) gave on hydrolysis 2 : 3 : 4 : 6-tetramethyl galactose, and a liquid trimethyl glucose which on conversion into the glucoside gave the characteristic crystalline 2 : 3 : 4-tri-

* This formula was indexed as 2 : 3 : 5-trimethylglucose on the basis of the older formula for glucose.

methyl β-methylglucoside, m. p. 94°, identical with that previously isolated from methylated raffinose.

For the purpose of this comparison, we have again submitted hendecamethyl raffinose to hydrolytic cleavage, and have separated the trimethyl glucose fragment from the other methylated hexoses by extraction with chloroform. The tetramethyl derivatives of galactose and γ-fructose are removed by this solvent, as is also a small proportion of the trimethyl glucose, but the greater proportion of the trimethyl glucose remains in the aqueous solvent. Isolation of this residue and conversion into the glucoside gave again the characteristic crystalline 2 : 3 : 4-trimethyl β-methylglucoside, m. p. 93—94°. Finally, we have prepared melibiose from raffinose and have transformed this sugar into heptamethyl methylmelibioside, which is a crystalline compound. It has previously been described by Schlubach and Rauchenberger (*Ber.*, 1925, **58**, 1184) as forming needles, m. p. 98·5° (after twice crystallising from light petroleum). Ordinarily, the substance is found to melt at about this temperature, but two further crystallisations raised the melting point to 101—103°, and this specimen gave no depression of m. p. when mixed with the methylated melibiose isolated as a by-product during the methylation of raffinose (see above). On repeated crystallisation, however, the m. p. was raised to 106—107°, and the specific rotation was correspondingly diminished from $[\alpha]_D + 113°$ to $[\alpha]_D + 97·8°$ (in water).

It thus appeared that the material had been contaminated with what was probably an α-form of heptamethyl methylmelibioside; indeed a portion of the material was isolated (m. p. 122—123°).* As is usual, however, in the methylation of sugars with methyl sulphate and alkali, the major bulk of the product was isolated as the β-form. This was hydrolysed with dilute mineral acid and the mixture of tetramethyl and trimethyl hexoses was separated by taking advantage of the greater ease with which a tetramethyl hexose may be extracted from aqueous solution by chloroform. In this way this tetramethyl hexose was recovered from the solution in chloroform and was shown to contain crystalline 2 : 3 : 4 : 6-tetramethyl galactose, m. p. 71—73°; $[\alpha]_D + 149·4° \longrightarrow 116·9°$ (yield 50%). The portion remaining in the aqueous solution represented about 35% of the weight of the original methylated melibiose. The latter product was liquid, and was transformed into a mixture of the α- and β-methylglucosides by heating with methyl-alcoholic hydrogen chloride. This mixture of the two stereoisomeric

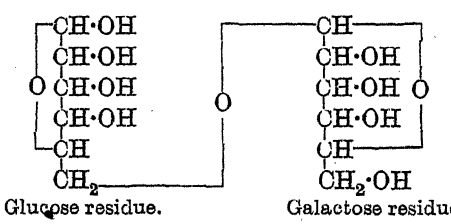
* A mixture of the α- and β-forms (m. p. 82°; $[\alpha]_D + 145°$) also gave on hydrolysis 2 : 3 : 4-trimethyl glucose, isolated as the β-methylglucoside, m. p. 94° (yield, 28%).

forms of the glucoside distilled completely and underwent spontaneous crystallisation immediately. Of the total yield of distillate, 13—15% by weight was collected as the characteristic 2 : 3 : 4-trimethyl β-methylglucoside, which on recrystallisation gave m. p. 92°. The liquid portion of the distillate doubtless contained a further quantity of this crystalline material.

Since the original distillate represented an equilibrium mixture of α- and β-forms, the former of which is liquid, it will be recognised that the whole of the product cannot be isolated as the crystalline β-variety. Proof of the identity of the glucoside was established by mixed melting-point determinations with specimens of the 2 : 3 : 4-trimethyl β-methylglucoside which had previously been isolated (*a*) from heptamethyl methylgentiobioside, (*b*) from methylated amygdalin, (*c*) from methylated raffinose, references to which preparations are given in the experimental section of this paper. Furthermore, a specimen of the crystalline 2 : 3 : 4-trimethyl β-methylglucoside has been specially prepared for the present comparison in the following way.

The 6-triphenylmethyl glucose (Helferich, Moog, and Jünger, *Ber.*, 1925, **58**, 872) was completely methylated with methyl iodide and silver oxide, and thereafter the triphenylmethyl residue was removed by hydrolysis. The specimen of 2 : 3 : 4-trimethyl β-methylglucoside obtained in this way was identical in all respects with the above material obtained from methylated melibiose.

(II.)



Glucose residue. Galactose residue.

The evidence adduced from these experimental results does not appear to be capable of any simple interpretation other than that in melibiose there is present a glucose residue which is attached through its (6) position to the reducing group of the galactose residue, and therefore the formula (II) previously advanced by Haworth and Leitch (J., 1918, **113**, 188) as modified by the introduction of the new oxide-ring formulæ for the hexoses (Charlton, Ha[illegible]orth, and Peat, J., 1926, 89) is fully supported.

In the interim Zemplén (*Ber.*, 1927, **60**, 923) has advanced new structural formulæ for melibiose and raffinose, differing from those which have been assigned by us to these sugars. The experimental evidence on which Zemplén bases his conclusions is the failure, which

he records, to isolate a phenylosazone from the galactoarabinose obtained by degradation of melibiose. Haworth and Long (this vol., p. 544) have already pointed out that an element of danger attaches to this method of proof, and indeed, the trimethyl hexose which would be expected on the basis of Zemplén's formula for melibiose would be 2 : 4 : 6-trimethyl glucose. Fortunately, we had a specimen of this sugar, and its glucoside, in our possession for the purpose of comparison, and it may be definitely stated that this sugar could not be isolated from the products of hydrolysis of methylated melibiose.

Discussion of Results.

The fact that melibiose is slowly attacked by the enzymes present in emulsin (Fischer and Armstrong, *Ber.*, 1902, **35**, 3144) has been widely interpreted in the literature as evidence for the classification of this sugar as a glucose β-galactoside. The specific enzyme for the hydrolysis of melibiose is, however, that occurring in bottom yeast, which is designated melibiase.

The observation of Helferich and Rauch (*Ber.*, 1926, **59**, 2655) casts doubt on the presence of a β-biose linking in this sugar, and these authors suggest that the configuration assigned may be incorrect. The following comparisons of the specific rotations may be considered in the discussion of this point.

	$[\alpha]_D$.		$[\alpha]_D$.
Maltose (β-glucose-α-glucoside)	+118°	Cellobiose (β-glucose-β-glucoside)	+16°
		Gentiobiose (β-glucose-β-glucoside)	−11
Melibiose	+124	Lactose (β-glucose-β-galactoside)	+35

Those disaccharides which possess indisputably a β-biose linking have low rotations as compared with maltose, which has an α-biose linking, and melibiose displays a rotation corresponding to that of maltose. Moreover, α-methylgalactoside has $[\alpha]_D$ + 178·8°, whilst the specific rotation of β-methylgalactoside is ± 0°. If melibiose were a glucose β-galactoside, its rotation, on the analogy of the relationship of lactose to gentiobiose, should be nearly zero, whereas if it were a glucose α-galactoside the rotation should be comparable with that of maltose, which is the case.

It has previously been remarked (Haworth and Leitch, J., 1919, **115**, 813) that there is some resemblance to maltose in the behaviour of melibiose, and this resemblance may be due to a stereochemical rather than a structural relationship.

On Hudson's method of representation (*J. Amer. Chem. Soc.*,

1916, **38**, 1566) the rotations of the disaccharides could each be divided into three parts as follows :

	[α]D, β-form.	[α]D, β-form octa-acetate.
1. Lactose β-galactose<glucose< Ga − L_1 + R_1 ...	+ 35°	− 4°
2. Cellobiose β-glucose<glucose< G − L_1 + R_1.....	+ 16	−15
3. Maltose α-glucose<glucose< G + L_1 + R_1	+118	+63

From (2) and (3) by subtraction L = 51 for the β-forms of the sugar, and this value is in excellent agreement with the value L = 50 for the lactonyl grouping in the simple glucosides and galactosides (recalculated for mol. wt. 342 for disaccharides). Furthermore, Hudson has pointed out that the value + 19° for (β-lactose–β-cellobiose) agrees excellently with his calculated value + 18°.

As further confirmation of these relationships, we may consider lactose and maltose.

By subtraction
$$118 - 35 = G - Ga + 2L$$
$$83 = G - Ga + 102$$
$$\text{or } Ga - G = 19$$
(Hudson's calc. value = 18.)

In view of the above, it would appear possible to take the value L = 51 and use it in the case of melibiose, at least as a very fair approximation.

If the rotation of melibiose be compared with that of gentiobiose, we have the following possible cases :

	[α]D, β-form.
1. Melibiose an α-biose α-galactose<glucose< Ga + L + R_2 ...	+124°
2. Gentiobiose β-glucose<glucose< G − L + R_2	− 11
3. Melibiose a β-biose β-galactose<glucose< Ga − L + R_2.....	+124

(*a*) Melibiose as an α-biose.

From (1) and (2) the difference in rotation between the β-forms of melibiose and gentiobiose = 135 or Ga − G + 2L. From Hudson's observed values for the experiment, Ga − G = 19, and L calculated as above and confirmed = 51.

Hence calculated diff. = 121,
observed ,, = 135.

(*b*) If melibiose is a β-biose, from (2) and (3) the difference in rotation = Ga − G.

Hence calculated diff. = 19,
observed ,, = 135.

Therefore presumably melibiose must be an α-biose.

Similar calculations based on the observed figures for the octa-acetates of the disaccharides, gentiobiose, melibiose, and the synthetic 6-glucosido-β-galactose of Helferich and Rauch (*loc. cit.*),

also favour the presence of an α- rather than a β-biose linking in melibiose, and the agreement between the observed and the calculated value for the expression Ga′ — G′ (107 and 113) is also fairly close, whereas the calculated figure for melibiose as a β-biose is 11.

Occasion may here be taken to correct a misprint in the paper by Haworth, Hirst, and Ruell (*loc. cit.*), where the m. p. of 2 : 3 : 4-trimethyl β-methylglucoside is given as 74° instead of 94°. That this is a typographical error is seen from the context, since this product was described as being identified by a mixed m. p. determination with the same product from amygdalin biose (gentiobiose), described in the paper immediately preceding it in the Journal (Haworth and Wylam, *loc. cit.*), where the m. p. is given as 94·5°. Again, the m. p. 94°, and not 74°, is given in the abstract of Haworth, Hirst, and Ruell's paper published about the same date (*J. Soc. Chem. Ind.*, 1923, **42**, 1139); and is also given as 94° in the preliminary notice of papers to be read at the meeting on November 15th, 1923. These facts appear to have escaped the knowledge of Irvine and Macdonald (J., 1926, 1507), who on the basis of this misprint criticise the formula we have applied to raffinose.

Experimental.

Melibiose was obtained from raffinose by fermentation of the latter with top yeast containing a small quantity of malt sprouts as recommended by Hudson (*J. Amer. Chem. Soc.*, 1915, **37**, 2734), and the resulting disaccharide was identified as melibiose by the melting point and specific rotation of the octa-acetate.

Methylation.—To melibiose (22 g.), dissolved in 100 c.c. of water, 56 c.c. of sodium hydroxide solution (30%) and 38 c.c. of methyl sulphate were added at 30° over a period of 3 hours. By cautious and simultaneous addition of these reagents the solution was not permitted to become alkaline until the sugar had been deprived of its reducing activity. Thereafter 28 c.c. of the alkali were added, the temperature was raised to 70°, and the remaining portions of the reagents (making in all 196 c.c. of 30% sodium hydroxide and 107 c.c. of methyl sulphate) were admitted slowly. For example, lots of 14 c.c. of alkali and 7·6 c.c. of methyl sulphate were simultaneously admitted during a period of 25 minutes, with vigorous stirring. Finally, the solution was heated at 100° for an hour, then cooled, stirring being continuous during the separation of sodium sulphate. Over-night, more sodium sulphate separated. This was filtered off and washed with chloroform, and the filtrate was extracted four times with more chloroform. The latter extracts yielded 15 g. of syrupy product. The aqueous residues were neutralised, evaporated,

and extracted with alcohol, and the portion of partly methylated melibiose which was more soluble in water was thus recovered (10 g.).

The combined products were again submitted to the action of methyl sulphate and alkali, and to ensure complete methylation the products from this treatment were twice methylated with Purdie's reagents.

The material isolated by following this procedure was a viscid syrup which crystallised almost completely on nucleation with a specimen of heptamethyl methylmelibioside which had been isolated during the earlier experiments on the methylation of raffinose. The crude solid (yield, over 20 g.) was recrystallised from light petroleum several times (Found: OMe, 54·3. Calc., 54·7%). The initial m. p. of the crude methylated melibiose, 85—90°, was raised considerably by repeated crystallisation from light petroleum, and after four or six such recrystallisations the crystals had m. p. 101—103° and showed $[\alpha]_D$ + 113·8° in water ($c = 1·22$). Ordinarily, this might have been regarded as a pure specimen of heptamethyl β-methylmelibioside, and Schlubach and Rauchenberger (*Ber.*, 1925, **58**, 1184) describe the substance as melting at 98·5°. This material gives correct analyses, but it seemed to us doubtful whether it was stereochemically pure. By recrystallising this five times, the crystals showed a higher melting point, 106—107°, and a diminished rotation, $[\alpha]_D$ + 97·8° in water ($c = 1$), + 85·0° in ethyl alcohol ($c = 1·1$) (Found: C, 52·8; H, 8·5; OMe, 53·5. Calc.: C, 52·9; H, 8·4; OMe, 54·7%). It was thus evident that the purification had resulted in the removal of the α-stereoisomeride, and elsewhere we describe what appears to be the α-variety, m. p. 122—123°.

Hydrolysis.—A solution of 2 g. of heptamethyl methylmelibioside in 150 c.c. of 5% hydrochloric acid was heated at 95—100°. The rotations in a 1 dm. tube showed $[\alpha]_D$ 1·34° (initial); 1·22° (1 hr.); 1·21° (2½ hrs.); 1·18° (4 hours); 1·18° (5½ hours). The solution was neutralised with silver carbonate, filtered, and treated with charcoal to remove traces of silver, and the concentrated filtrate was extracted five times with chloroform. This extract on evaporation gave 1 g. of a syrup which crystallised spontaneously after 2 weeks; m. p. 71—73° (after crystallisation from light petroleum). It was recognised as 2 : 3 : 4 : 6-tetramethyl galactose by direct comparison and mixed melting-point determination with the specimen prepared from lactose by Haworth and Long (this vol., p. 544), $[\alpha]_D$ + 149·4° ⟶ 116·9°.

The anilide also was prepared; m. p. 192—193°, unchanged in admixture with an authentic specimen of tetramethyl galactose

anilide. The portion of the hydrolysed product which was not extracted by the chloroform was recovered on evaporation of the aqueous solution under diminished pressure. This was a liquid (0·65 g.) representing the trimethyl hexose fragment of the hydrolysed product. A small quantity of this material was also present in the chloroform extract already mentioned, containing principally the tetramethyl galactose fragment, so that approximately equal weights of the latter and of the trimethyl hexose comprised the total products of hydrolysis (weighing 1·65 g.).

The syrupy trimethyl hexose was dissolved in dry methyl alcohol containing 0·5% of hydrogen chloride and heated at 100—110° for 10 hours. Neutralisation of the solution with freshly precipitated silver carbonate and removal of the solvent led to the isolation of a glucosidic substance, having no action on Fehling's solution and distilling under 0·01 mm. almost completely from a bath heated to 110—130°. The colourless distillate crystallised spontaneously in the receiver, but the crystals were contaminated with liquid, which was drained on porous tile. Evidently both a liquid α-form and a crystalline β-form of the glucoside were present. The crystalline product was purified by means of light petroleum and obtained as a mat of interlaced needles, m. p. 92°, and this m. p. was not depressed by admixture with 2 : 3 : 4-trimethyl β-methylglucoside which had previously been isolated from (*a*) methylated gentiobiose (Haworth and Wylam, J., 1923, **123**, 3120), (*b*) methylated amygdalin (Haworth and Leitch, J., 1922, **121**, 1921), (*c*) methylated raffinose (Haworth, Hirst, and Ruell, *loc. cit.*), (*d*) a specimen obtained from 6-triphenylmethyl glucose (compare Helferich, Moog, and Jünger, *loc. cit.*) which had been methylated with methyl iodide and silver oxide and hydrolysed to remove the triphenylmethyl residue.

Hydrolysis of Hendecamethyl Raffinose.—A specimen of this derivative of raffinose remained over from the previous research and it was considered desirable to obtain confirmation of the identity of the trimethyl glucose fragment occurring in the mixture of hydrolytic products obtained by digesting hendecamethyl raffinose with dilute mineral acid. Accordingly, 3·7 g. were hydrolysed at 85° with 150 c.c. of 5% hydrochloric acid. The subsequent treatment of the products followed the usual procedure, but instead of separating the mixture of partly methylated hexoses by distillation, the neutralised aqueous solution of these was extracted several times with chloroform. This treatment completely removed the fructose and galactose fragments, and the aqueous solution was now evaporated under diminished pressure, giving rise to the trimethyl hexose, which appeared as a syrup. Digestion of this syrup with methyl-alcoholic hydrogen chloride (containing 0·53% HCl) during

10 hours at 110° gave, on neutralisation followed by evaporation of the solvent, a glucoside which distilled completely, and the distillate afterwards crystallised, giving long, colourless needles, m. p. 92·5°. This was identified as 2 : 3 : 4-trimethyl β-methylglucoside by admixture with the authentic specimens previously referred to (Found : C, 50·7; H, 8·5. Calc. : C, 50·8; H, 8·5%).

Isolation of Heptamethyl Methylmelibioside from the Products of the Methylation of Raffinose [with D. A. RUELL].—On fractional distillation of crude hendecamethyl raffinose prepared by repeated methylation of raffinose (Haworth, Hirst, and Ruell, J., 1923, **123**, 3125), a syrupy product (b. p. 185—190°/0·03 mm.; n_D 1·4660) was obtained. This solidified after some days and purification by means of light petroleum yielded crystals, m. p. 78°, which after further recrystallisation melted at 101—103° and had $[\alpha]_D$ + 113·8° in water (c = 1·22). Analytical data indicated that this crystalline substance was a completely methylated disaccharide (Found : C, 53·3; H, 8·4; OMe, 51·8. Calc. : C, 52·9; H, 8·4; OMe, 54·6%). On admixture of this compound with an authentic specimen of heptamethyl methylmelibioside, m. p. 101°, the melting point showed no depression.

Hydrolysis and Identification of Cleavage Products.—Heptamethyl methylmelibioside was hydrolysed under conditions identical with those applied in the case of methylated raffinose (Haworth, Hirst, and Ruell, *loc. cit.*) and the process was complete after 24 hours :

Time in hours	0	6	13	18	24	30
$[\alpha]_D$	+106°	93·9°	88·3°	82·3°	73·6°	74·0°

A syrupy, amber-coloured product was obtained which was soluble in dry ether. The syrup was digested in ethyl-alcoholic solution with excess of aniline for 3 hours, and on removal of the solvent and of free aniline, a semi-solid mass remained. Drainage on porous tile gave crystals which, purified by means of ethyl alcohol, appeared as silky needles, m. p. 192—193°, identical in all respects with a specimen of tetramethyl galactose anilide previously prepared from methylated raffinose or lactose, in admixture with which the m. p. was not depressed.

The syrup separating after removal of the crystals of tetramethyl galactose anilide was dissolved in alcohol, and the solution clarified with charcoal; on concentration a further small quantity of crystals separated, which were identical with the anilide mentioned above. Complete evaporation of the solution gave a viscid syrup, which was dissolved in a little aqueous alcohol and rendered faintly acid to Congo-paper with hydrochloric acid. The solution was steam-distilled in order to remove traces of aniline, and the aqueous residue

was again clarified and evaporated to dryness in a vacuum. The product obtained from this treatment was dissolved in methyl alcohol containing 0·5% of hydrogen chloride, and heated in sealed tubes at 110° for 10 hours. Thereafter the solution was neutralised with silver carbonate, and the filtrate evaporated. Extraction of this residue with dry ether yielded a viscid liquid, which distilled at 0·01 mm. from an oil-bath heated at about 140°. The distillate was a colourless liquid which partly crystallised on nucleation with 2 : 3 : 4-trimethyl β-methylglucoside. The crystals were collected and washed in light petroleum; they then melted at 90—91°. Recrystallisation from light petroleum gave m. p. 93—94°. On admixture with a specimen of 2 : 3 : 4-trimethyl β-methylglucoside obtained from a previous research on the constitution of gentiobiose, no depression of melting point was observed.

ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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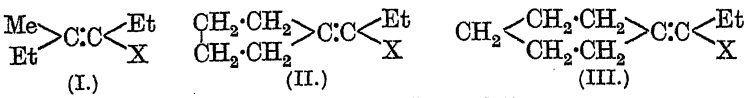
CCIII.—*The Chemistry of the Three-carbon System. Part XII. The Effect of Positive Substituents in the α-Position on the Tautomerism.*

By GEORGE ARMAND ROBERT KON and BINDIGAWAVALE TIRUMALACHAR NARAYANAN.

IN studying the influence of substituents on three-carbon tautomerism, we examined first the effect produced by a group in the α-position, that is, attached to the carbon atom bearing the negative activating group. The effect of introducing a negative or activating group in this position has been discussed (Kon and Speight, J., 1926, 2727); the effect of a positive group on the mobility and point of equilibrium of three-carbon systems is described below.

Theoretically, the effect of a positive substituent in the α-position should be a general diminution of the mobility of the system—a phenomenon frequently observed in keto-enol systems, glutaconic esters, etc. The effect on the position of equilibrium is less easy to forecast, because it is probably made up of more than one factor, both polar and steric in nature. It must be assumed that the polar effect diminishes that due to the activating group; and as this favours the αβ-phase, it is to be expected that the βγ-phase will be favoured by the presence of an α-alkyl group. A phenyl group should behave in the same way from the electronic point of view, but the strong tendency to conjugation exhibited by this group (Linstead and Williams, J., 1926, 2735; Johnson and Kon, *ibid.*,

p. 2748) would probably neutralise this tendency, and it would be expected that the αβ-phase in α-phenylated systems would possess considerable stability. We were not able to study this case owing to difficulty in preparing suitable material for investigation; we have, however, examined a number of systems bearing an ethyl group on the α-carbon atom and belonging to several representative types, namely, acids, ketones, and nitriles of the general types (I), (II), and (III).



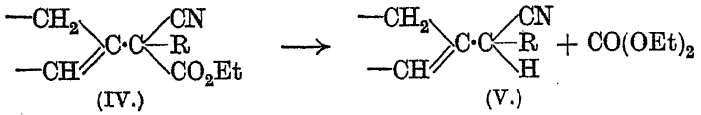
(I.) (II.) (III.)

X = CO_2H, COMe, or CN.

The properties of the first two groups of compounds are in full agreement with theoretical considerations. The mobility of the systems appears to be less than that of the parent substances; indeed, Birch, Kon, and Norris (J., 1923, **123**, 1361) had failed to condense α-ethyl-Δ^1-*cyclo*hexenylacetone with ethyl sodiomalonate and concluded that this ketone did not react in the αβ-phase. That statement requires revision, for the condensation does proceed, although it requires a considerable time for completion. The mobility of the system in ketones of this series is, however, still considerable, because only one substance, having in every case the βγ-structure, is obtained under the conditions of the Blaise–Maire synthesis from either the αβ- or the βγ-acid; the conversion of αβ-acids into their βγ-isomerides on treatment with alkali is actually unexpectedly rapid. These facts indicate that the βγ-forms of the compounds in question are even more favoured than those of the parent (unsubstituted) compounds and that the mobility of the system is not very greatly affected.

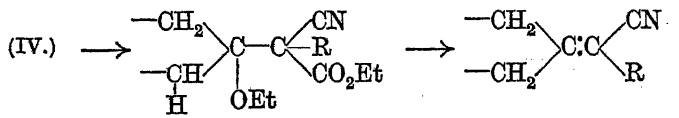
It is, therefore, all the more surprising to find that the α-substituted nitriles, of which several have been prepared by Birch and Kon (J., 1923, **123**, 2440), constitute a sharp contrast to the acids and ketones just mentioned. They are invariably obtained in the αβ-form, and no direct evidence had until lately been obtained of the existence of a βγ-phase, although it is abundantly proved that unsubstituted nitriles, such as *cyclo*hexenylacetonitrile, exist in the βγ-form, but can also react in the αβ-form (compare Birch and Kon, *loc. cit.*). Whilst this difference appears at first to be in contradiction with theoretical considerations, it is capable of a ready explanation. The reaction by which α-substituted nitriles are produced involves the elimination of ethyl carbonate from the corresponding cyano-esters under the influence of alcoholic sodium ethoxide and it has been shown by Ingold and Thorpe (J., 1919,

115, 143) to proceed in many cases in the presence of very small amounts of the reagent. The cyano-esters from which they are produced have necessarily a $\beta\gamma$-unsaturated structure (IV) and it has been assumed hitherto that the $\beta\gamma$-form (V) of the nitrile would be produced at first :



(IV.) (V.)

This view of the mechanism is, however, incorrect; the only way in which the system can reacquire its mobile hydrogen atom, and one which at the same time explains the ready occurrence of such reactions, consists in the addition of the elements of alcohol to the double bond, the hydrogen becoming attached to the γ-carbon atom; the system then loses ethyl carbonate with the formation of an $\alpha\beta$-double bond :



This possibility was overlooked in the original paper (Birch and Kon, *loc. cit.*), but it would appear that the scheme now suggested is of general application and that $\alpha\beta$-unsaturated compounds are always produced by the elimination of ethyl carbonate from fully substituted but potentially tautomeric systems (compare Thole and Thorpe, J., 1911, **99**, 2191; Thorpe, J., 1912, **101**, 871; Feist, *Annalen*, 1922, **428**, 25).

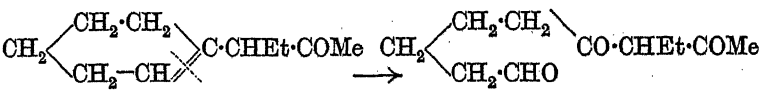
The $\alpha\beta$-compounds so produced can, of course, pass into the $\beta\gamma$-forms if they are sufficiently mobile under the conditions of the experiment; this is, apparently, not the case for the nitriles under discussion. The probable reason for this lack of mobility was suggested by Prof. R. Robinson (private communication), who pointed out that the retarding effect of the α-alkyl group on the mobility of the system was likely to be greater the weaker the activating group on which mobility ultimately depends; it would be greatest in a system activated by a weak group such as CN (compare Bradley and Robinson, J., 1926, 2356). For this reason, α-substituted nitriles are probably static or nearly so and are therefore isolated in the $\alpha\beta$-form, although this may not be the most stable. Experiments have been undertaken to confirm this view : the $\beta\gamma$-isomeride of *cyclo*hexylidenebutyronitrile has already been prepared and found to differ from the $\alpha\beta$-compound; its properties are now under investigation.

The α-substituted nitriles can be hydrolysed by means of alcoholic sulphuric acid to the corresponding αβ-unsaturated esters (or ester containing a high proportion of the αβ-compound), but these cannot be further hydrolysed to the acids without undergoing conversion into the βγ-form.

Some experiments were carried out to ascertain the positions of equilibrium between the αβ- and βγ-acids in the presence of alkali of various concentrations, but an exact estimate was impossible owing to the insufficient analytical methods available at the time. Conversion of the acids into their amides shows, however, that the equilibrium is so much on the side of the βγ-compound that the presence of the αβ-isomeride cannot be recognised with certainty. The acids are mostly liquids and extremely difficult to purify, and therefore do not lend themselves well to investigation by the analytical methods recently developed by Linstead (this vol., p. 355).

The semicarbazones of the α-substituted ketones are isolated in only one form in the ordinary way; a small amount of a second form can, however, be obtained in all cases by previously treating the ketone with cold sodium ethoxide for 40 hours.

The oxidation of ketones of this group is always difficult. Ozonisation, however, gives definite evidence of the βγ-form of these substances; in every case an oil, giving a deep colour with ferric chloride, is formed, evidently according to the scheme



We have, moreover, succeeded in oxidising one of the ketones to the corresponding acid by means of hypobromite, the βγ-acid being the sole product obtained.

EXPERIMENTAL.

1-*Hydroxy*-α-*ethyl*cyclo*hexaneacetic Acid*.—The ester was obtained by the Reformatski reaction as described by Wallach (*Annalen*, 1908, **360**, 44); the yield (55%) was slightly improved by adding the magnesium in several portions. The hydrolysis of the ester was difficult and considerable fission into ketone and butyric acid always occurred. The best method was as follows: 100 G. of the ester were added to a hot solution of 100 g. of potassium hydroxide in 100 c.c. of water; 100 c.c. of methyl alcohol were then added gradually and the mixture was refluxed for 2—3 hours. The solution was freed from alcohol under reduced pressure, diluted, extracted with ether, and acidified with ice-cold 30% sulphuric acid. The *acid* thus

liberated was extracted with ether, dried, and distilled under reduced pressure, some 24 g. boiling at 167—170°/16 mm. This fraction was a viscous oil with a strong odour of butyric acid; $d_4^{18\cdot8°}$ 1·0010, $n_D^{18\cdot8°}$ 1·46798 (Found: C, 64·7; H, 10·05. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%. Found for the *silver* salt: Ag, 36·9. $C_{10}H_{17}O_3Ag$ requires Ag, 36·9%).

α-Ethyl-Δ^1*-cyclohexenylacetic Acid.*—The hydroxy-ester on dehydration with phosphorus oxychloride or potassium hydrogen sulphate yielded ethyl α-ethyl*cyclo*hexenylacetate (Wallach, *loc. cit.*), b. p. 112—116°/15—18 mm., $d_4^{18\cdot2°}$ 0·862624, n_D 1·45593; $[R_L]_D$ 57·09 (Calc., 56·72) (Found: C, 63·8; H, 9·9. Calc.: C, 63·5; H, 10·2%). The acid obtained from it on alkaline hydrolysis had b. p. 154—156°/20 mm., $d_4^{20\cdot6°}$ 1·01528, $n_D^{20\cdot6°}$ 1·47014 (Found: Ag in silver salt, 39·2. Calc.: Ag, 39·3%). Wallach's hydrobromide, m. p. 106—107°, was readily obtained. The *amide*, prepared by leading dry ammonia into a benzene solution of the acid chloride, was recrystallised from dilute methyl alcohol and had m. p. 115—116° (Found: C, 71·3; H, 10·4. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·2%). The p-*toluidide* was similarly obtained and had m. p. 115° after crystallisation from alcohol (Found: N, 5·6. $C_{17}H_{23}ON$ requires N, 5·4%).

A small quantity of the acid was ozonised in dry chloroform solution, and the ozonide shaken with cold water for 20 minutes. The aqueous solution gave a deep violet colour with ferric chloride; 20% sulphuric acid was then added and the product steam-distilled. Adipic acid was identified in the residue in the flask.

*α-Ethyl*cyclo*hexylideneacetic Acid.*—This acid was prepared by treating the hydroxy-acid with acetic anhydride in the usual manner and isolated from the steam distillate by means of ether. On distillation, some hydrocarbon, a fraction, b. p. up to 160°/20 mm., and one, b. p. 164—166°/20 mm., were obtained, the last being the almost pure αβ-acid. This had $d_4^{19\cdot0°}$ 1·01831 and n_D 1·47977 (Found in the silver salt: Ag, 39·3. Calc.: Ag, 39·3%). The yield was poor (20%).

An attempt was also made to prepare the acid from the ester obtained by hydrolysis of α-*cyclo*hexylidenebutyronitrile, b. p. 129°/20 mm.* (Farrow and Kon, J., 1926, 2128), as described by Harding, Haworth, and Perkin (J., 1908, **93**, 1949); the crude ester had b. p. 120—124°/20—23 mm., $d_4^{18\cdot8°}$ 0·936298, $n_D^{18\cdot8°}$ 1·46827, $[R_L]_D$ 58·22 (Calc., 56·72). The ester on careful alkaline hydrolysis gave a mixture of acids in which the βγ-acid predominated.

The *chloride*, prepared by the action of thionyl chloride, boiled

* The b. p. of this substance was omitted in the original description (*loc. cit.*).

at 110—112°/20 mm. and gave an *amide*, m. p. 104—105° after crystallisation from dilute alcohol, in which it is more soluble than the βγ-amide; a mixture of the two amides melted at 94—98° (Found: C, 71·3; H, 10·6%). The p-*toluidide* melted at 104°.

The acid did not give well-defined oxidation products with permanganate; on treatment with ozone in chloroform solution, traces of *cyclo*hexanone and some adipic acid were obtained. The product obtained by treating the ozonide with cold water did not give a colour with ferric chloride.

Equilibration Experiments.—3·36 G. of α-ethyl*cyclo*hexylideneacetic acid (the αβ-acid) were boiled with a large excess of 20% sodium hydroxide solution for ½ hour. The product was isolated in the usual way and separated into a neutral and an acid portion by means of sodium hydrogen carbonate. The neutral compound (0·5—0·7 g.) was evidently a lactone; it was converted into the silver salt of the corresponding hydroxy-acid (Found: Ag, 37·0. Calc. for $C_{10}H_{17}O_3Ag$: Ag, 36·9%). The acid recovered from the bicarbonate solution was converted into the amide, which melted at 106—108° (mixed m. p. with the βγ-amide, 106—110°) in the crude state and at 114° after two crystallisations.

The experiment was repeated with 50% alkali. A larger quantity (1—1·2 g.) of the lactone was obtained, the amide of the acid melted at a lower temperature, and by repeated crystallisation some 10% of the αβ-amide could be isolated from it, in addition to the βγ-amide, m. p. 114°.

α-Ethyl-Δ^1-*cyclo*hexenylacetic acid (the βγ-acid) also was treated with 20% potassium hydroxide solution. About 0·5 g. of the lactone was isolated; the amide obtained melted at 113—114° after two crystallisations; the αβ-amide was present only in traces.

α-*Ethyl*cyclo*hexenylacetone.*—This ketone was obtained in 50—55% yield by the action of zinc methyl iodide on the chloride of *either* the αβ- or the βγ-acid; the latter reaction has already been carried out by Birch, Kon, and Norris (*loc. cit.*). It is most conveniently prepared by the ethylation of *cyclo*hexenylacetone in the presence of sodium (Kon, J., 1926, 1792) or sodium ethoxide. The semicarbazone has m. p. 177—182° (crude) and 185° after crystallisation (Found: C, 64·1; H, 9·3; N, 19·0. Calc.: C, 64·6; H, 9·4; N, 18·8%). The ketone regenerated from it had $d_4^{18·6°}$ 0·92011 and n_D 1·46798 and gave the same semicarbazone on treatment with semicarbazide.

The ketone (3·32 g.) was kept for 40 hours in a solution of 0·46 g. of sodium in 10 c.c. of alcohol. The ketone was recovered (2·6 g.) and converted into the semicarbazone (1·2 g.), which melted at 167—180°. On recrystallisation from alcohol, this gave 0·9 g.

m. p. 185°; the mother-liquor on dilution gave a crop, m. p. 172—176°. After two more crystallisations, 0·1 g. was obtained, m. p. 175—176° (mixed m. p. with compound of m. p. 185°, 167—172°).

A solution of the ketone (2·24g.) in acetic acid at −4° was saturated with hydrogen bromide and poured into water after 15 minutes. The brown oil obtained was isolated by means of ether, the ether removed, and the bromo-ketone warmed on the steam-bath with aqueous sodium carbonate for 15 minutes. The regenerated ketone was converted into the semicarbazone, which melted at 185° after one crystallisation; no other semicarbazone appeared to be formed.

Attempts were made to alkylate the ketone in the presence of "molecular" sodium or sodium ethoxide, but no trace of alkylation product was obtained.

The ketone (5·4 g.) was heated over-night with ethyl malonate (5·2 g.) and sodium (0·82 g.) in 20 c.c. of alcohol. The product was cooled and poured into water, neutral impurities were removed with ether, and the aqueous layer was strongly acidified and again thoroughly extracted with ether. On removing the ether, a solid (6·5 g.) was obtained which gave a blood-red colour with ferric chloride, and melted at 76—77° after crystallisation from benzene and petroleum; it was hydrolysed by boiling it for 3 hours with 20% potassium hydroxide solution. The product was acidified, warmed for another hour, and shaken with ether. The dried extract gave on evaporation a solid, which was recrystallised from acidified water and again from dilute alcohol; lustrous needles, m. p. 159—160°, of cyclo*hexane*spiro-2-*ethyl*cyclo*hexane*-3 : 5-*dione* were thus obtained (Found: C, 74·8; H, 9·9. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·6%).

Oxidation of α-*Ethyl*cyclo*hexenylacetone*.—The ketone (2·5 g.) was suspended in a solution of 1·2 g. of potassium hydroxide in 10 c.c. of water and kept at 0° while 0·8 c.c. of bromine was gradually added with shaking; the mixture was kept at 0° over-night. A part of the ketone remained unchanged; from the alkaline liquid an acid was obtained (1 g.) which was converted into the amide (m. p. 108—112°; 113—114° after crystallisation); this was identified as the βγ-amide (α-ethyl-Δ^1-*cyclo*hexenylacetamide) by direct comparison.

No definite products were obtained on oxidation of the ketone with potassium permanganate; with ozone, an ozonide was formed which decomposed when shaken with cold water. The product, which gave a deep violet colour with ferric chloride, was mixed with 20% sulphuric acid and distilled in steam, but no definite products except adipic acid could be identified.

Ethyl 1-*Hydroxy*-α-*ethyl*cyclo*pentaneacetate*.—This ester was prepared from *cyclo*pentanone as was its higher homologue from *cyclo*-

hexanone, some 40 g., b. p. 127—137°/20—25 mm., being obtained from 1 g.-mol., in addition to 20 g. each of high and low fractions (Found: C, 66·5; H, 9·8. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%). The *acid* was obtained in 42% yield, b. p. 157—160°/23 mm., $d_4^{20·5°}$ 1·01232, $n_D^{20·5°}$ 1·43869, $[R_L]_D$ 44·55 (Calc., 44·65) (Found: C, 62·6; H, 9·5. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%. Found in silver salt: Ag, 38·8. $C_9H_{15}O_3Ag$ requires Ag, 38·7%).

α-Ethyl-Δ^1*-cyclopentenylacetic Acid.*—This βγ-acid could not be prepared by the usual method involving the dehydration of ethyl 1-hydroxy-α-ethyl*cyclo*pentaneacetate and hydrolysis, because the hydroxy-ester remained practically unchanged after treatment with potassium hydrogen sulphate and with anhydrous oxalic acid, whilst phosphorus oxychloride gave a very small yield of an impure ester accompanied by tarry by-products. Thionyl chloride also was unsatisfactory. The hydroxy-acid (44 g.) was boiled with 250 c.c. of 20% sulphuric acid for 2 hours, the product distilled in steam, and the distillate extracted with ether and divided into neutral (8 g.) and acid (15 g.) constituents. The latter consisted of an oil, b. p. 138—142°/15 mm., in addition to about 1 g. of a solid acid, m. p. 80—81° (the αβ-acid). The oily βγ-acid has a strong odour of butyric acid, $d_4^{17·4°}$ 1·01909, $n_D^{17·4°}$ 1·47525, $[R_L]_D$ 42·65 (Calc., 42·75) (Found: C, 70·5; H, 8·7. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%. Found in the silver salt: Ag, 41·4. $C_9H_{13}O_2Ag$ requires Ag, 41·3%). The *chloride*, prepared by means of thionyl chloride, has b. p. 96—98°/20 mm.; the *amide* obtained from it was appreciably soluble in water and formed lustrous needles, m. p. 102—103°, from dilute alcohol (Found: C, 70·2; H, 10·1. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%).

The acid readily adds on bromine in ether or acetic acid, but the *bromide* is unstable; the *hydrobromide* also was prepared in acetic acid solution, but could not be obtained solid.

*α-Ethyl*cyclo*pentylideneacetic Acid.*—This αβ-acid was prepared from the hydroxy-acid (70 g.) by the method described on p. 1540. The first runnings were liquid; thereafter 14 g. of a solid, m. p. 80—81° after crystallisation from ether–petroleum, were obtained (Found: C, 70·4; H, 9·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%). The liquid by-product gave three fractions on distillation; 4 g. boiled below 100°/16 mm., 6 g. up to 158°, and 8 g. at 158—162°. The *chloride* had b. p. 102—106°/16—18 mm.; the *amide* formed pearly plates, m. p. 97° (mixed m. p. with the βγ-amide, 78—82°), from aqueous alcohol, and was less soluble than the βγ-isomeride (Found: C, 70·7; H, 10·1. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%). The *bromide* was unstable; the *hydrobromide* could not be obtained solid.

The *nitrile* was obtained in the same way as the higher homologue (Farrow and Kon, *loc. cit.*), the yield being 65%. It had b. p. 116—118°/20 mm., $d_4^{21\cdot7°}$ 0·923586, $n_D^{21\cdot7°}$ 1·47555, $[R_L]_D$ 41·22 (Calc., 40·90). The nitrile was hydrolysed to the *ethyl* ester, which had b. p. 116—118°/25 mm., $d_4^{19\cdot5°}$ 0·936298, $n_D^{19\cdot5°}$ 1·47417, $[R_L]_D$ 54·65 (Calc., 52·10). Both ester and nitrile gave *cyclo*pentanone on oxidation with ozone. Hydrolysis of the ester led to a mixture of acids in which the βγ-acid predominated.

α-*Ethyl*-Δ^1-cyclo*pentenylacetone*.—This βγ-ketone was obtained in about 60% yield by the action of zinc methyl iodide on α-ethyl-*cyclo*pentenylacetyl chloride; the yield from the αβ-chloride was much lower (40%). The semicarbazone formed plates, m. p. 166—167°, from dilute alcohol, and was identical with that prepared from the ethylated parent ketone (Kon and Linstead, J., 1925, **127**, 821). The ketone regenerated from it had b. p. 94°/15 mm., $d_4^{19\cdot5°}$ 0·917685, $n_D^{19\cdot5°}$ 1·45942, $[R_L]_D$ 45·32 (Calc., 45·72).

The ketone was treated with sodium ethoxide exactly as described on p. 1541; the semicarbazone obtained from the product contained about 10% of a more soluble form, m. p. 143—145°.

Addition and removal of hydrogen bromide produced no change, and attempts to introduce another alkyl group failed.

The ketone condensed readily with ethyl sodiomalonate, the reaction being complete in 3 hours, but neither the dihydroresorcinol ester nor its hydrolysis product could be obtained solid; the liquid products showed the usual reactions of their class with ferric chloride, etc. A small amount of the diketone was oxidised with hypobromite and the resulting dibasic acid (α-*ethyl*cyclo*pentane*-1 : 1-*diacetic acid*) was analysed in the form of its *silver* salt (Found: Ag, 50·8. $C_{11}H_{16}O_4Ag_2$ requires Ag, 50·5%).

The ketone formed an ozonide, which was decomposed by cold water to an oil giving an intense colour with ferric chloride but from which no definite compounds could be obtained on hydrolysis. Oxidation with permanganate also was inconclusive.

β-*Hydroxy*-β-*methyl*-α-*ethylpentanoic Acid*.—The ester was prepared from methyl ethyl ketone as before; the reaction started very slowly, but the yield was good, being 127 g., b. p. 106—108°/18 mm., together with 20 g. of a lower fraction which can be used for preparing the βγ-ester (Found: C, 63·4; H, 10·9. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·8%). On hydrolysis, a 50% yield of the *acid* was obtained as an oil, b. p. 132—136°/20 mm. (Found for the *silver* salt: Ag, 40·6. $C_8H_{15}O_3Ag$ requires Ag, 40·5%).

β-*Methyl*-α-*ethyl*-Δ^β-*pentenoic Acid*.—The preceding hydroxy-ester gave a 70% yield of ethyl β-methyl-α-ethyl-Δ^β-pentenoate, b. p. 84—88°/20 mm., $d_4^{19\cdot2°}$ 0·93160, $n_D^{19\cdot2°}$ 1·43618, $[R_L]_D$ 48·67 (Calc.,

49·34) on dehydration with phosphorus oxychloride, and about a 50% yield with potassium hydrogen sulphate. The *acid*, obtained on hydrolysis in 66% yield, was a liquid with a penetrating smell, b. p. 122—126°/20 mm., $d_4^{20\cdot4°}$ 0·95884, $n_D^{20\cdot4°}$ 1·45113, $[R_L]_D$ 39·90 (Calc., 40·23) (Found for the *silver* salt: Ag, 43·3. $C_8H_{13}O_2Ag$ requires Ag, 43·4%). The *chloride* had b. p. 76—78°/18—20 mm.; the p-*toluidide* formed needles, m. p. 102—104°, from methyl alcohol.

The acid in dry chloroform was treated with ozone, and the ozonide decomposed with water; acetaldehyde was formed in quantity and was identified by means of β-naphthol as usual (compare Kon and Linstead, J., 1925, **127**, 616).

β-*Methyl*-αβ-*diethyl*-Δ^{α}-*pentenoic Acid.*—This acid, prepared in poor yield from β-hydroxy-β-methyl-αβ-diethylpentanoic acid by means of acetic anhydride, had b. p. 126—130°/15—18 mm., $d_4^{20\cdot4°}$ 0·95930, $n_D^{20\cdot4°}$ 1·45193, $[R_L]_D$ 39·94, and was probably still contaminated with some of the hydroxy-acid, although the silver salt gave correct figures on analysis (Found: Ag, 43·3. Calc.: Ag, 43·4%). The *chloride* had b. p. 86—90°/20 mm.; a small lower fraction (b. p. 72—76°) also was obtained. The p-*toluidide* crystallised from methyl alcohol, in which it is more soluble than the βγ-toluidide, in plates, m. p. 112—113° (mixed m. p. 87—89°). The *hydrobromide* was unstable.

δ-*Methyl*-γ-*ethyl*-Δ^{δ}-*hexen*-β-*one.*—This ketone was obtained in good yield from β-methyl-α-ethyl-Δ^{β}-pentenoyl chloride. The *semicarbazone* formed lustrous needles or plates, m. p. 163—164°, from methyl or ethyl alcohol (Found: C, 61·3; H, 9·3. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6%). The *ketone* regenerated from it had b. p. 72—74°/16 mm., $d_4^{19\cdot7°}$ 0·85068, $n_D^{19\cdot7°}$ 1·43908, $[R_L]_D$ 43·30 (Calc., 43·38). The *same* ketone was also obtained, although in poorer yield, from the αβ-chloride. The ketone was oxidised in dry chloroform solution with ozone; the ozonide on decomposition gave acetaldehyde, which was identified as before.

The ketone was treated with cold sodium ethoxide for 48 hours (p. 1541). The semicarbazones prepared from the product consisted for the most part of δ-methyl-γ-ethyl-Δ^{δ}-hexen-β-one semicarbazone, m. p. 163—164°, but contained also about 7% of a semicarbazone which melted, after repeated crystallisation, at 151—152°. A mixture of the two semicarbazones melted at 138—149°. After treatment with hydrogen bromide, the original ketone also gave a very small amount of a semicarbazone, m. p. 148—149°.

Attempts to alkylate the ketone were unsuccessful. The ketone condensed readily with ethyl sodiomalonate to a liquid ester which gave an intense colour with ferric chloride; the dihydroresorcinol

obtained on hydrolysis of the ester did not solidify and was not further examined.

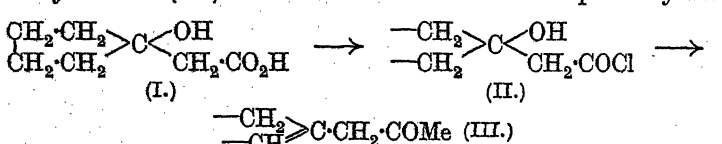
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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, April 29th*, 1927.]

CCIV.—*The Preparation of Unsaturated Ketones from the Chlorides of Hydroxy-acids.*

By GEORGE ARMAND ROBERT KON and BINDIGAWAVALE TIRUMALACHAR NARAYANAN.

IN seeking to extend the methods by which ketones of the type of *cyclo*hexenylacetone are obtained, we were led to examine the action of zinc methyl iodide and of zinc ethyl iodide on the chlorides produced directly from hydroxy-acids, without previously converting these into unsaturated acids. This object had already been partly achieved by Blaise and Maire (*Ann. Chim. Phys.*, 1908, **15**, 556), who acetylated the hydroxy-acids before converting them into their chlorides; they found, however, that this method failed when applied to β-disubstituted acids, as these, instead of being acetylated, were dehydrated to a mixture of unsaturated acids. The work of Darzens (*Compt. rend.*, 1911, **152**, 1314, 1601) also made it appear probable that the action of thionyl chloride or phosphorus pentachloride on hydroxy-acids would lead to dehydration. Actually, it was found that cyclic β-hydroxy-acids gave each a mixture containing, in addition to varying quantities of the chlorides of the two possible unsaturated acids, a considerable proportion of its own chloride, from which it could be regenerated. These chlorides, on treatment with zinc methyl iodide, gave ketones identical with those obtainable from the chlorides of the unsaturated acids. Thus, *cyclo*pentanolacetic acid (I) gave a chloride (II) from which, on treatment with zinc methyl iodide, a fair yield of *cyclo*pentenylacetone (III) was obtained. This ketone is probably best



prepared by the process now described. The corresponding ethyl ketones were obtained only in very poor yield, owing to the simul-

taneous formation of the ethyl ester of the $\beta\gamma$-unsaturated acid. The production of this ester is at present unexplained. Experiments carried out with a few α-hydroxy-acids sufficed to show that the chlorides were highly unstable and had no practical value for the synthesis of ketones; a small quantity of tetrahydroacetophenone was, however, prepared from *cyclo*hexanolcarboxylic acid.

EXPERIMENTAL.

1-Hydroxy*cyclo*pentane-1-carboxylic acid (43 g.) was treated with excess of thionyl chloride in the cold. When the frothing had subsided, the mixture was warmed for 20 minutes, and the excess of reagent removed in a vacuum. The chloride decomposed during distillation even under 3·5 mm.

In another experiment the acid (43 g.) was gradually added to 69 g. of phosphorus pentachloride and the mixture was warmed for 30 minutes, but no attempt was made to purify the chloride. A portion of it gave, on treatment with formic acid, the original acid, m. p. 103°. The crude chloride was then treated with zinc methyl iodide, but only a very small amount of a disagreeable-smelling, non-ketonic liquid was obtained.

1-Hydroxy*cyclo*hexane-1-carboxylic acid behaved exactly like the lower homologue both with phosphorus pentachloride and with thionyl chloride. The action of zinc methyl iodide on the crude chloride gave a very poor yield of a substance which combined with semicarbazide, giving tetrahydroacetophenone semicarbazone (m. p. and mixed m. p. 216—217°). The action of zinc ethyl iodide gave no ketonic product, but a small amount of an oil, b. p. 110—114°/20 mm., which appeared to be ethyl tetrahydrobenzoate.

A chloride could not be obtained from hexahydromandelic acid.

1-Hydroxy*cyclo*pentane-1-acetic acid (48 g.), after treatment with excess of thionyl chloride, gave on distillation 5 g. of a chloride, b. p. 85—87°/17 mm., and 16 g. (30%) of another chloride, b. p. 98—110°/17 mm. The former gave, when poured into formic acid, *cyclo*pentenylacetic acid, m. p. 51—52°, and when treated with aniline, cyclo*pentenylacetanilide*, which crystallised from methyl alcohol in silky needles, m. p. 98° (Found: C, 77·3; H, 7·9. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%). The higher-boiling chloride gave a mixture of anilides from which cyclo*pentylideneacetanilide* could be isolated in nodules, m. p. 152—153°, after several crystallisations (Found: C, 77·2; H, 7·6. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%). On pouring the chloride into formic acid, a gummy acid was obtained from which the original acid, m. p. 77°, was isolated after repeated treatment with benzene–petroleum.

The action of zinc methyl iodide (1/3 mol.) on the higher-boiling

chloride prepared from 48 g. of the hydroxy-acid gave 8 g. of a ketone. The semicarbazone prepared from this was separated by crystallisation into three forms, m. p. 138°, 189°, and 121—122°, respectively, the last being apparently a constant-melting mixture of the other two. These were the two semicarbazones of *cyclo*pentenylacetone (Kon, J., 1921, **119**, 823); the one of m. p. 138° was formed in greater quantity.

The action of zinc ethyl iodide on the same chloride gave an ester, probably ethyl *cyclo*pentenylacetate; no ketone appeared to be formed.

The action of thionyl chloride on 1-hydroxy*cyclo*hexane-1-acetic acid (53 g.) gave 35 g. of a product, b. p. 95—98°/15—17 mm., consisting mainly of the chloride of the hydroxy-acid, as it gave the original acid on being poured into formic acid. The action of aniline on it gave a mixture from which the *anilides* of *cyclo*hexenylacetic acid, needles, m. p. 117° (Found: C, 77·9; H, 8·2%) and of *cyclo*hexylideneacetic acid, m. p. 138—139° (Found: C, 78·4; H, 7·8. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9%), were obtained. The anilide of the hydroxy-acid appears to be indefinite.

The acid chloride from 53 g. of the acid was treated with zinc methyl iodide; 17 g. of *cyclo*hexenylacetone, b. p. 102—104°/20 mm., identified by means of the semicarbazone, were obtained.

The reaction was repeated with zinc ethyl iodide, but the yield of ketone was very much less, partly owing to the formation of ethyl *cyclo*hexenylacetate in some quantity. The ketone gave two semicarbazones, m. p. 153° and 184—185° respectively. The former is identical with the semicarbazone of Δ^1-*cyclo*hexenylmethyl ethyl ketone (Kon, J., 1926, 1797), whilst the latter is isomeric with it and is probably the semicarbazone of the $\alpha\beta$-form [Found: (for the form of low m. p.) C, 63·2; H, 9·2; (for the form of high m. p.) C, 62·9; H, 9·5. $C_{10}H_{17}ON_3$ requires C, 63·2; H, 9·0%].

1-Hydroxy-α-ethyl*cyclo*pentane-1-acetic acid (see preceding paper) (29 g.) gave 17 g. of a chloride, b. p. 99—102°/25 mm. The chloride gave with ammonia a mixture of the $\alpha\beta$- and the $\beta\gamma$-unsaturated amide, in the proportion of 1 : 2; a third amide, melting indefinitely at about 70°, was also obtained but could not be purified. The action of zinc methyl iodide (1/6 mol.) on 15 g. of the acid chloride gave 8·5 g. of a liquid, b. p. 103—105°/25—27 mm., from which the semicarbazone of α-ethyl-Δ^1-*cyclo*pentenylacetone, m. p. 166—167° after crystallisation, was readily obtained.

1-Hydroxy-α-ethyl*cyclo*hexane-1-acetic acid (see preceding paper) (30 g.) gave 22 g. of a chloride, b. p. 122—127°/20 mm. This, on treatment with ammonia, gave an amide, m. p. 108—110°, which, on repeated crystallisation, melted at 113—114° and proved identical

with the βγ-unsaturated amide; a trace of another amide, m. p. 108—109°, distinct from both the αβ- and the βγ-amide, was also obtained. By the action of zinc methyl iodide (1/6 mol.) on the acid chloride (20 g.), 9 grams of a liquid, b. p. 122—124°/20 mm., were obtained. This contained a considerable amount of unsaturated ester in addition to α-ethyl*cyclo*hexenylacetone, which was isolated in the form of its semicarbazone, m. p. 185°.

β-Hydroxy-β-methyl-α-ethylpentanoic acid gave a 70% yield of chloride, b. p. 75—90°/20—25 mm., on treatment with thionyl chloride. It consisted mainly of the chlorides of the two unsaturated acids, as evidenced by the *p*-toluidides obtained from it, but a third, indefinite, product was also formed, probably derived from the hydroxy-acid. The yield of ketone, b. p. 78—82°/25 mm., from the acid chloride was poor; it readily gave the characteristic semicarbazone, m. p. 163—164°, identical with that previously obtained from the unsaturated acids.

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CCV.—*The Chemistry of the Three-carbon System. Part XIII. The Effect of Bulky Substituents and of the* cyclo*Heptane Group on the Tautomerism.*

By GEORGE ARMAND ROBERT KON and CECIL JOHN MAY.

THE effect of a positive substituent in the α-position on the tautomerism of a three-carbon system has been discussed (this vol., p. 1536); that of bulky substituents in the β-position is now described.

To obtain a strictly comparable series it would be necessary to work with β-substituted pentenoic acids, because it has already been shown that the βγ-phase does not become stable until the γ-carbon atom carries at least a methyl group, as in the acid $CHMe{:}CMe{\cdot}CH_2{\cdot}CO_2H$ (Kon and Linstead, J., 1925, **127**, 616). The next member of the series is diethylacrylic acid; this and its βγ-isomeride were studied by Kon and Linstead. Other β-substituted pentenoic acids are, however, difficult to prepare owing to lack of accessible initial materials, and a further difficulty is that there are in every case two possible βγ-acids, according as the double bond is in the shorter or the longer chain. We have therefore

limited the present experiments to two compounds, namely, ββ-dipropyl- and ββ-di*iso*butyl-acrylic acids (I; R = Et and Pr^{β}, respectively) and their βγ-isomerides (II), to which these objections do not apply.

(I.) $\begin{matrix}CH_2R\\CH_2R\end{matrix}\!\!>\!C{:}CH\cdot CO_2H$ $\qquad$ $\begin{matrix}CH_2R\\CHR\end{matrix}\!\!>\!C\cdot CH_2\cdot CO_2H$ (II.)

The γ-substituent in these acids may be expected to have some effect on the stabilities of the αβ- and βγ-forms. From considerations based on the electronic theory (compare Allan, Oxford, Robinson, and Smith, J., 1926, 401; Ingold, Shoppee, and Thorpe, *ibid.*, p. 1477), it is deduced that the presence of a positive substituent in the γ-position would favour the βγ-phase, whilst in the β-position this substituent would have little effect. These effects will be comparatively insignificant if it is merely a question of substituting a larger for a smaller group. Should, however, steric factors have any considerable influence on the equilibrium, then it might be expected that such a substitution would produce a very definite effect; and this will be shown to be the case. The tendency of a double bond to migrate from the αβ- to the βγ-position appears to be connected with the alteration of the normal tetrahedral angle about the β-carbon atom (J., 1926, 2727); the case may be compared with the formation of a three-membered ring by ring-chain tautomerism (Bains and Thorpe, J., 1923, **123**, 1206; Deshapande and Thorpe, J., 1922, **121**, 1430).

(A) $\begin{matrix}R\\R'\end{matrix}\!\!>\!C\!<\!\begin{matrix}CO\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}$ $\longrightarrow$ $\begin{matrix}R\\R'\end{matrix}\!\!>\!C\!<\!\begin{matrix}C(OH)\cdot CO_2H\\CH\cdot CO_2H\end{matrix}$

(B) $\begin{matrix}R\\R'\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH\cdot CO_2H\\\cdots\end{matrix}$ $\longrightarrow$ $\begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}CH\cdot CO_2H$

The formation of an αβ-double bond in (B) will be analogous to the formation of a three-membered ring from (A), an increase in bulk of the groups R and R′ in each case facilitating the formation of the "ring" system. In (B) there are three possible positions for the double bond; the four valencies of the central carbon atom must be regarded as asymmetrically directed, the angle between any two of them being determined by the resultant of two opposing steric factors. The double bond should therefore be most readily produced in the direction of the smallest group (this does not apply to the methyl group owing to the comparative instability of a terminal methylene group, unless specially stabilised as in itaconic acid). In straight-chain acids where R = H (*e.g.*, the pentenoic acids), the steric effect is negligible and the αβ-phase is the more stable; as the bulk of R increases, the βγ-form is stabilised. When, however, both R and R′ increase to such an extent that the group

$-CH{\cdot}CO_2H$ becomes relatively small, the equilibrium again tends towards the αβ-form. It is doubtless for this reason that Johnson and Kon (J., 1926, 2748) found the equilibrium in the β-ethylcinnamic acids to be on the side of the βγ-form (76 : 24), whilst in the next higher acids the equilibrium was already of the order 50 : 50. Again, in the *gem*-diethyl series, the equilibrium is strongly on the side of the βγ-form (95 : 5, according to Linstead; this vol., p. 355). The two pairs of acids now studied fall well into line, for the equilibrium in the dipropyl series is 67 : 33 in favour of the βγ-form, whilst in the di*iso*butyl series it is already 51 : 49, thus illustrating the effect of bulky groups.

In the behaviour of the cyclic acids, other factors come into play. The tendency of a ring to acquire a double bond—which is a measure of the stability of the βγ-phase—is difficult to correlate with the distortion of the normal tetrahedral angle in these rings; *e.g.*, the stability of the βγ-phase increases but slightly from the *cyclo*pentane (85 : 15; Linstead, private communication) to the *cyclo*hexane series (88 : 12; Linstead, *loc. cit.*), although the difference in the distortion of the normal tetrahedral angle is considerable; it decreases appreciably in the *cyclo*heptane series, the equilibrium being about 75 : 25 in favour of the βγ-phase. In other words, the *cyclo*heptane ring shows less tendency to acquire a double bond than either of the smaller rings.

ββ-Dipropylacrylic acid (I; R = Et) has been described by Albitzki (*J. pr. Chem.*, 1884, **30**, 209) as a solid, m. p. 80—82°; this was analysed only in the form of variously hydrated salts. Reformatski (*J. Russ. Phys. Chem. Soc.*, 1890, **22**, 44) obtained the acid only as a liquid; the dibromide he prepared from it differed from Albitzki's dibromide. We have prepared the acid, which melts at 9°, by dehydrating ββ-dipropylhydracrylic acid with acetic anhydride and have characterised it by the formation of an amide, m. p. 72°; its structure was confirmed by oxidation. Albitzki's method of dehydrating the hydroxy-acid could lead only to the βγ-acid, and did so in our hands. The βγ-acid obtained thus and in other ways was always contaminated with αβ-acid; all the preparations were liquid (all the βγ-acids studied up to the present melt at lower temperatures than the αβ-acids; the converse holds for the amides), and the acid itself has not yet been obtained pure, although a pure ester and an amide (m. p. 120—121°) have been prepared. The di*iso*butyl compound proved even more discouraging in this respect, as inseparable mixtures of the two acids were obtained by all the available methods.

cyclo*Heptylideneacetic acid*, on the other hand, was readily obtained as a solid, m. p. 54°, giving a dibromide, m. p. 125°.

Baker and Ingold isolated a small quantity of a liquid which they described as the αβ-acid and characterised by the formation of a dibromide, m. p. 125°; this must have been the αβ-dibromide. This is surprising, because, under the experimental conditions used by Baker and Ingold, the αβ-acid is rapidly isomerised to the extent of 75% into the liquid βγ-isomeride, previously described by Wallach as the αβ-form (*Annalen*, 1902, **314**, 157) and yielding a dibromide, m. p. 103—104°. It must be assumed that Baker and Ingold's hydrolysis was carried out so rapidly that complete equilibration of the αβ-acid first produced could not take place and the mixture contained enough αβ-acid to give its dibromide.

Experimental.

ββ-Dipropylacrylic Acid (I; R = Et).—The reaction between dipropyl ketone and ethyl bromoacetate with magnesium proceeded well in benzene solution, the yield of ethyl ββ-dipropylhydracrylate, b. p. 139°/15 mm., being 50%. The acid was obtained from the ester, on hydrolysis in the usual manner, as a thick oil which could not be distilled even at 2 mm.

On dehydration with acetic anhydride (Wallach, *Annalen*, 1907, **353**, 288), it yielded ββ-dipropylacrylic acid (I), which is a colourless, practically odourless oil, b. p. 144°/17 mm.; this set, on freezing, to a mass of crystals which melted at 9°. It had $d_4^{20\cdot0°}$ 0·93624, $n_D^{20\cdot0°}$ 1·46350, $[R_L]_D$ 45·97 (calc. 44·84) (Found: C, 68·9; H, 10·4. Calc. for $C_9H_{14}O_2$: C, 69·1; H, 10·3%. Found in the silver salt: Ag, 41·1. Calc.: Ag, 41·1%). The *chloride* had b. p. 128°/25 mm. and gave with ammonia in ethereal solution the *amide*, which separated from light petroleum in long, flattened needles, m. p. 72°. The p-*toluidide* crystallised from dilute methyl alcohol in needles, m. p. 82·5°. The *ethyl* ester, prepared through the acid chloride, had b. p. 108—109°/14 mm., $d_4^{18\cdot0°}$ 0·89284, $n_D^{18\cdot4°}$ 1·44923, $[R_L]_D$ 55·35 (calc., 54·19). Both the ester on treatment with ozone and the acid on oxidation with permanganate gave good yields of dipropyl ketone, which was identified by means of its semicarbazone, m. p. 133°.

β-Propyl-Δ^β-hexenoic Acid (II; R = Et).—The ethyl ester was readily obtained pure by heating ethyl ββ-dipropylhydracrylate with a 20% excess of phosphorus pentoxide under reduced pressure; it gradually distilled and was purified by redistillation (yield 75%); b. p. 116—118°/25 mm., $d_4^{25\cdot0°}$ 0·89264, $n_D^{25\cdot0°}$ 1·43778, $[R_L]_D$ 54·13. It gave no trace of dipropyl ketone on oxidation. The acid was prepared by the hydrolysis of this ester, also by dehydrating the hydroxy-acid by means of 20% sulphuric acid (compare Farrow and Kon, J., 1926, 2138; Albitzki, *loc. cit.*; Reformatski, *loc. cit.*),

50% sulphuric acid, or phosphorus trichloride. In the last case, the acid (3 mols.) in ether was gradually added to rather more than 2 mols. of the chloride with cooling, and the mixture was kept for 24 hours and finally warmed on the steam-bath until no more hydrogen chloride was evolved. The acid obtained by these processes had b. p. 138—140°/22 mm. and 126—128°/11 mm., and the following properties:

(1; 20% H_2SO_4) $d_4^{22°}$ 0·93400, n_D 1·45593, $[R_L]_D$ 45·43.
(2; 50% H_2SO_4) $d_4^{16°}$ 0·93813, n_D 1·45833, $[R_L]_D$ 45·42.
(3; PCl_3) $d_4^{19°}$ 0·93692, n_D 1·45753, $[R_L]_D$ 45·42.

All the samples thus showed a slight exaltation, and gave on oxidation small quantities of dipropyl ketone. Many methods of purification were tried without success. The *chloride* boiled at 107°/30 mm. and gave a mixture of amides on treatment with ammonia. This was resolved into its constituents by repeatedly washing it with petroleum, in which only the αβ-amide was freely soluble. The residue, after several crystallisations from benzene–petroleum, consisted of the pure *βγ-amide*, m. p. 120—121°; it could be sublimed (Found: C, 69·5; H, 11·2. $C_9H_{15}ON$ requires C, 69·6; H, 11·1%).

Equilibration of the Acids.—The αβ- and the βγ-acid (in the latter case, the purest sample available) were each refluxed with ten times the calculated quantity of potassium hydroxide (20 or 60% solution) for 24 hours; the acid mixture was then isolated by Linstead's method (*loc. cit.*). The percentage of αβ-acid in the mixture was determined by Bougault's method (*Ann. Chim. Phys.*, 1908, **14**, 145) with the following results:

Equilibrium mixture from the αβ-acid: (a) 35·7%, (b) 33·0%.
„ „ βγ-acid: (a) 31·4%,

from which the mean figure is 33%. A discussion of the details of procedure is reserved for a future communication.

Attempts to Prepare the Acids by Other Methods.—An attempt to prepare the αβ-acid by elimination of hydrogen bromide from α-bromo-β-propylhexoic acid was abandoned because the bromo-acid could not be obtained free from unbrominated material. The preparation was carried out as follows: Dipropylcarbinol (100 g.), prepared in 50% yield by the method followed by Grignard (*Compt. rend.*, 1901, **132**, 336) for preparing di*iso*butylcarbinol and in 75% yield by reducing dipropyl ketone with sodium wire in wet ether (Kurtz, *Annalen*, 1876, **181**, 205), was refluxed for 4—5 hours with 600 g. of hydrobromic acid (*d* 1·5) free from sulphuric acid. The bromide, b. p. 161—165°/749 mm. (slight decomp.), 88°/64 mm.,

thus obtained in 50% yield, was condensed with ethyl sodiomalonate in alcohol in the usual manner, a good yield of *ethyl hydrogen iso*heptylmalonate, b. p. 168°/35 mm., being obtained in the place of the diethyl ester (Found: C, 62·9; H, 9·4. $C_{12}H_{22}O_4$ requires C, 62·6; H, 9·6%). The acid was readily obtained on alkaline hydrolysis; it refused to solidify and therefore was distilled, a good yield of β-*propylhexoic acid* being collected as a colourless liquid with a not unpleasant odour, b. p. 144°/30 mm. (Found: C, 68·2; H, 11·3. $C_9H_{16}O_2$ requires C, 68·3; H, 11·5%). The acid was converted into its chloride and brominated, crystals of an unstable bromo-acid chloride being obtained; these could not be freed from unbrominated material and rapidly decomposed on distillation or on exposure to the air.

Attempts to obtain the corresponding β-bromo-acid (hydrobromide of dipropylacrylic acid) were also unsuccessful.

ββ-*Diisobutylacrylic Acid.*—Di*iso*butyl ketone (*iso*valerone) was condensed with ethyl bromoacetate; the yield of ethyl β-hydroxy-ββ-di*iso*butylpropionate was always poor, the best (35%) being obtained by carrying out the condensation in ether and warming the reaction product over-night; 30% of the ketone was recovered. The ester boiled at 138—140°/20 mm. and yielded a viscous liquid acid on hydrolysis. The hydroxy-acid could not be purified by distillation. It was dehydrated both with acetic anhydride and with dilute sulphuric acid, mixtures of unsaturated acids being obtained in every case; b. p. 144—149°/20 mm. (Found: C, 71·5; H, 10·6. $C_{11}H_{18}O_2$ requires C, 71·7; H, 10·9%). The properties of different preparations were as follows ($[R_L]_D$ calc., 54·06):

Source of acid.	*t.*	*d.*	n_D.	$[R_L]_D$ obs.
(1) Dehydr. by Ac_2O	21°	0·92530	1·46091	54·60
(2) ,, ,, ,, ...	21	0·92488	1·46111	54·65
(3) ,, ,, ,, ...	26	0·91885	1·46982	54·88
(4) ,, ,, dil. H_2SO_4	19	0·92141	1·46723	54·46
(5) KOH on (1)	18·5	0·92609	1·46131	54·56
(6) ,, (4)	20	0·91660	1·46603	54·51
(7) Regen. from acid chloride...	17·5	0·92782	1·46144	54·54

Equilibration. This was carried out as described on p. 1553, and the percentage of αβ-acid in the mixture determined as before; the mean value was 49% of αβ-acid.

cyclo*Heptylideneacetic Acid.*—Suberone, obtained in 40% yield from thorium suberate by Ruzicka's method (*Helv. Chim. Acta*, 1926, **9**, 515), was converted into ethyl *cyclo*heptanolacetate (Wallach, *loc. cit.*) as before, 30 g. being obtained from 56 g. of suberone, 16 g. of which were recovered. This quantity of ester gave 20 g. of hydroxy-acid which did not solidify.

The acid (20 g.) was boiled with 35 c.c. of acetic anhydride for

3—4 hours, and the unsaturated acid isolated by distillation in steam, 5 g. of solid being obtained in addition to a small amount extracted from the head and tail fractions; it formed colourless needles, m. p. 54° (Found: C, 69·6; H, 9·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·2%).

A small quantity of the acid was treated with dry ozone in chloroform solution; the ozonide on decomposition gave an 80% yield of suberone (weighed as semicarbazone).

αβ-*Dibromo*cyclo*heptylacetic Acid.*—The αβ-acid (0·5 g.) was dissolved in 2 c.c. of acetic acid, 0·5 g. of bromine in acetic acid added, and the mixture left in an exhausted desiccator; crystals of the dibromide slowly separated. On recrystallisation from chloroform–petroleum colourless crystals, m. p. 125°, were obtained.

Δ^1-cyclo*Heptenylacetic Acid.*—The hydroxy-acid (15 g.) was refluxed for 3 hours with an excess of 10% sulphuric acid, and the unsaturated acid was distilled in steam and isolated by means of ether, the yield being 2·5 g. Its properties corresponded closely with those of Wallach's acid: b. p. 158—160°/18 mm., $d_4^{22°}$ 1·0382, $n_D^{22°}$ 1·49232, $[R_L]_D$ 43·09. When examined by Bougault's method, this acid was proved to contain 24% of αβ-acid.

βγ-*Dibromo*cyclo*heptylacetic Acid.*—The crude βγ-acid was converted into a dibromide under the same conditions as the αβ-acid; it crystallised only partly, the solid being the new dibromo-acid, which on crystallisation formed hard, colourless prisms, m. p. 103—104°. A mixture of this with the αβ-dibromide melted at about 79°. On standing, the βγ-dibromide gradually darkened and appeared to be converted into a bromo-lactone.

Equilibration. Experiments were carried out starting both with the αβ- and with the βγ-acid; the mean of several determinations gave the percentage of the αβ-acid in the mixture as 25·6.

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CCVI.—*Low Temperature Oxidation of Hydrocarbons.*

By JOHN STANLEY LEWIS.

IN his researches on the combustion of methane and ethane, Bone proved conclusively that reaction with oxygen takes place at temperatures well below the ignition point, the products being aldehydes,

water, etc. As a result of this work he put forward his hydroxyl theory (J., 1902, **81**, 535; 1903, **83**, 1074; 1904, **85**, 693, 1637; *Proc. Chem. Soc.*, 1905, **21**, 220). More recent work has shown that paraffin oils and waxes undergo oxidation at low temperatures, and the latter have been converted into fatty acids, but attention has been given also to the unsaturated hydrocarbons, especially diolefins, which are prevalent in "cracked" spirit. A review of the work on "Gasolines" is given by Brooks (*Ind. Eng. Chem.*, 1926, **18**, 1198). An advance has been made by Callendar (*Engineering*, February, 1927), who has proposed the theory that the initial step in the oxidation of paraffins at low temperatures is the formation of peroxides which decompose eventually into aldehydes, acids, water, etc.

The present paper contains an account of (*a*) a simple arrangement for determining the temperatures of initial oxidation of paraffin hydrocarbons at constant volume; (*b*) the influence of certain factors upon these temperatures; (*c*) a proposed mechanism of the reaction, which may be called the "primary dehydrogenation theory"; and (*d*) an attempt to apply this theory to account for the instability of paraffin hydrocarbons as measured by their ignition and detonation characteristics.

Experimental.

Molecular Weights at High Temperatures.—The determination of molecular weights by the Victor Meyer method at temperatures above 200° gives anomalous results for paraffins, the molecular weights decreasing as the temperature increases (Ormandy and Craven, *J. Inst. Petroleum Tech.*, Nov., 1925), as shown in Table I.

Table I.

Molecular-weight determinations (Ormandy and Craven).

Temp.	Heptane.	Shell.	Pratt's.	Benzene.
200°	102	100	97	77
220	73	96	96	76
250	79	98	95	78
265	74	80	78	75
275	70			
275 (plus piece of porous pot)	78			

The suggested explanation of this decrease is that chemical action of some kind has taken place causing an increase in the number of molecules, and the above workers attributed this partly to the cracking of the paraffins, and to partial combustion whilst the spirit remained in the liquid phase, vapours being affirmed to be more stable. Experiments conducted with coal-gas gave more normal results. The foregoing results have been disputed by some

workers, but they have been confirmed in this laboratory, and some of the results obtained for hydrocarbons other than paraffins are shown in Table II.

TABLE II.

Molecular-weight determinations of typical hydrocarbons.

Benzene.		Toluene.		*cyclo*Hexane.		Amylene.	
Temp.	*M.*	Temp.	*M.*	Temp.	*M.*	Temp.	*M.*
198°	78·6	187°	92	230°	85	200°	72
240	78·4	360	92	260	83	254	73
285	79·8	400	93	342	68	297	60
350	78·4	310 (in oxygen)	93	362	61	295 (in nitrogen)	72
360 (in oxygen)	78·8	385 (in oxygen)	93	400	73	303 (in nitrogen)	70
				400 (in oxygen)	Exploded.	310	65
				400 (in nitrogen)	85	355 (in oxygen)	Exploded.

The aromatic substances are apparently stable up to 400° in these experiments, whereas the olefin and the naphthene are affected by oxygen, but not by nitrogen, and their molecular weights are normal. This seems to discount the view that cracking takes place to any appreciable extent, and experiments are in progress on the lines described later to ascertain the exact temperatures at which the various hydrocarbons crack, and thus to obtain comparative values for their stability in the absence of oxygen. Increase in the expected volume of gas, *i.e.*, decrease in the measured molecular weight, is to be attributed to oxidation, but this oxidation can and does take place in the vapour phase, as will be shown later. It was observed also that the tubes used for weighing the liquid always contained films of gums or tarry deposits at the end of the experiments; these were light brown for low temperatures, and deepened to black tars as the temperature of experiment was increased. These gums are probably formed during cooling and are the condensation products of aldehydes.

The results of the earlier molecular-weight determinations were erratic and variable owing to the fact that the weights of liquid in each experiment differed, thus altering the ratios of hydrocarbon to oxygen and to the surface area of the Victor Meyer bulb. By using the same weighing tube throughout, with approximately equimolecular proportions of liquid for each temperature, and a large bulb, more concordant results were obtained, the observed molecular weights of hexane and octane decreasing gradually with rise of temperature above a certain limit. A fairly smooth curve was thus recorded for temperature–molecular weight (Fig. 1). The figures are in Table III.

TABLE III.

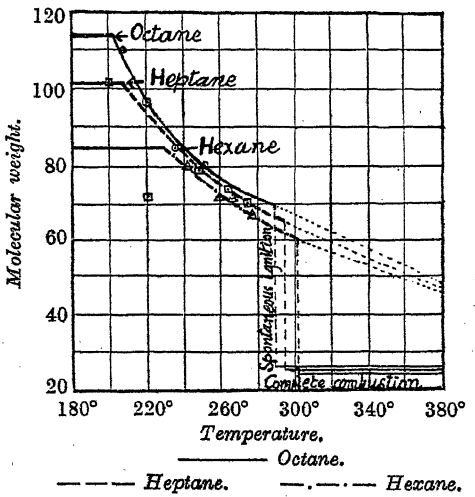
Molecular weights of paraffins, obtained by using constant proportions and conditions.

Hexane.		Heptane.*		Octane.	
Temp.	*M.*	Temp.	*M.*	Temp.	*M.*
200°	87	200°	102	180°	113
242	80	220	73	204	110
260	72	250	79	220	96
266	72	265	74	238	84
278	67	275	70	256	80

* Ormandy and Craven (*loc. cit.*).

These curves meet the horizontal line of constant molecular weight at a point corresponding approximately to the temperature of initial oxidation. At the other extreme the curves presumably intersect the horizontal lines corresponding to the molecular weights that would be attained if oxidation to water and carbon dioxide was complete; but before this temperature could be reached spontaneous ignition would take place, as indicated diagrammatically by the vertical lines. The above method is obviously unsatisfactory for determining the exact temperature at which oxidation is initiated, and the following simple method was used.

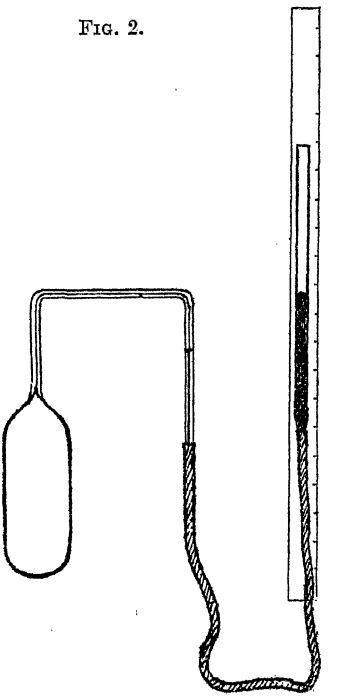
FIG. 1.



Constant-volume Method.—A known quantity of the liquid was enclosed in a large cylindrical bulb to which was attached a stout capillary tube connecting with a mercury manometer, as in the usual form of an air thermometer (Fig. 2). During the slow heating of the bulb, the manometer was raised constantly so that the mercury in the capillary tube was kept at a constant mark, the height of the mercury in the manometer plus the barometric pressure being the pressure of the mixture inside the bulb. Readings were taken at small intervals of temperature, and a pressure–temperature diagram was drawn. If no chemical action takes place the curve should follow approximately that of the gas laws, but in the case of the

paraffins there occurs a sudden rise or inflexion indicating chemical action. The temperature at which this rise occurs will be known as the " critical inflexion temperature " or the *C.I.T.* Typical curves are given in Fig. 3. Most of the hydrocarbons used in these experiments were either Kahlbaum preparations or of a purity complying with the recognised physical data. The following results were obtained: Pentane, 253°; hexane, 232°; octane, 198°. (It is possible to read the *C.I.T.*'s to within 1° or 2°.)

FIG. 2.



The initial part of the curve follows the air-thermometer curve approximately until the *C.I.T.* is reached, and once this is passed there is no rapid rise of pressure corresponding to a reaction with increased number of molecules. In fact, for some distance the curve does not differ much from the air curve, having a tendency to fall below rather than to rise above it, as though molecules were combining and becoming fewer in number. At much higher temperatures the curves revealed a progressive, but slow, decomposition. The form of the curve is unexpected, because the sudden rise at the *C.I.T.* denotes a reaction which is completed at this temperature, accompanied by an increase in the number of molecules. Hydroxyl or peroxide formation would cause a decrease in the number of molecules, and hence a depression in the curve, unless these oxygen derivatives were produced and decomposed at the same

FIG. 3.

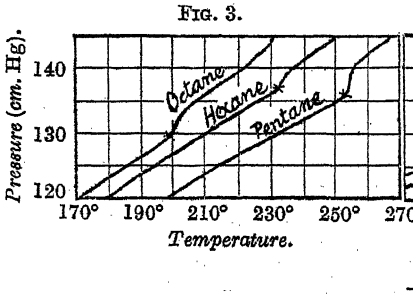
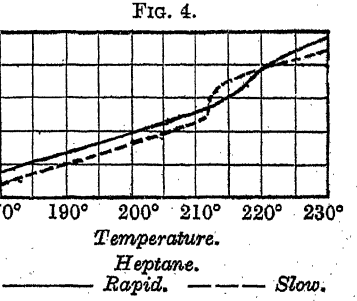


FIG. 4.



temperature. That the whole of this reaction takes place at the *C.I.T.* was proved by maintaining the temperature constant for some time, whereupon the pressure increased to a maximum and remained stationary.

It appears that for paraffin hydrocarbon–air mixtures there is a critical temperature at which rapid chemical action takes place with an increase in the number of molecules.

The critical temperature is dependent upon molecular weight, as seen in the results for pentane, hexane, and octane; but other factors influence it and the following experiments were instituted with a view to determine them.

Rate of Heating.—Two experiments were carried out with heptane, the rise of temperature in one case being extremely slow, and in the other about 1° per minute, the same bulb and equal quantities of liquid being used. The initial parts of the curves are parallel up to the *C.I.T.*, indicating that if chemical action has taken place the extent is the same for the two rates of heating. At the *C.I.T.* the rise for slow heating is more abrupt and is completed within 1° or 2°. That the reaction occurs with measurable velocity is shown by the curve for rapid heating (Fig. 4). In the case of pentane, which has a higher *C.I.T.*, the velocity of the reaction is greater, and with a rate of heating comparable with that denoted as "rapid" above, reaction is completed in a small range of temperature. It may be justifiably concluded that when one of these paraffin hydrocarbon–air mixtures is suddenly raised to a temperature well above the *C.I.T.* but below that of spontaneous ignition, as, *e.g.*, during sudden compression, the chemical change involved at the *C.I.T.* will take place almost instantaneously, giving rise to a pressure higher than the calculated, and also causing evolution of heat.

Concentration of the Vapour.—At first it was thought that concentration played no part, because the differences obtained were very small. To test this point, one bulb was used for a set of experiments in which gradually increasing weights of octane, and also hexane, were employed. The results for octane, depicted in Fig. 5, show that concentration affects the *C.I.T.* to a small but appreciable extent.

It is possible that chemical reaction begins below the *C.I.T.*, but if so, it must be very slight, because on heating some of the mixtures to temperatures below the *C.I.T.*, cooling, and reheating, the curves obtained were almost identical, but on occasions the contents of the bulb reduced a very weak solution of potassium permanganate. No "gumming" or coloration of the finally cooled liquid occurred, however, in any instance.

Atmosphere of Oxygen.—The curves for hydrocarbon–oxygen

mixtures were of the same nature as for air. The bulbs were filled with oxygen, a measured quantity of hydrocarbon was added, and pressure–temperature curves were determined as before. These curves varied only in the fact that the *C.I.T.* was more abrupt and completed within a smaller range of temperature (1—2°), showing that, whatever chemical change is taking place at the *C.I.T.*, the velocity is much greater in oxygen. The actual temperature, however, differed very little from that in a similar determination with air, and no more than would be expected from the change in the concentration ratio of vapour–oxygen to vapour–air.

A remarkable feature is that once the *C.I.T.* is passed, the contents of the bulb are apparently stable at least up to 450°, and have been heated to this point without explosion or spontaneous ignition occurring. Callendar, in his tube experiments, heated a paraffin–air mixture to 666° before ignition was reached, but slight explosions occurred at 516° with flashes of flame when the same mixture carried liquid drops of the hydrocarbon. It appears, therefore, that the liquid phase is more unstable than the vapour state, and the *C.I.T.* has some bearing upon this phenomenon. Spontaneous-ignition temperatures for liquid particles must give results which are far below those for complete vapour–air or oxygen mixtures.

Atmosphere of Nitrogen.—Hexane was heated in the apparatus, which had been filled with nitrogen, and up to 365° the pressure–temperature curve was normal and showed no inflexion. No gum was formed and the liquid remained colourless on cooling. On reheating, the pressure–temperature curve was practically identical with the first, thus confirming the work on molecular-weight determinations in nitrogen and the conclusion that no decomposition or "cracking" takes place. The sudden rise in pressure at the *C.I.T.* can only be attributed to oxidation of the paraffin–hydrocarbon molecules, accompanied by an increase in the final number of molecules.

Comparison of Isomerides.—Spontaneous-ignition tests are untrustworthy for making a comparison of the stability of the hydrocarbons in the presence of oxygen, and the recorded results are very variable. The method adopted in these experiments is suitable for comparing two isomerides if the *C.I.T.* is taken as the initial oxidation temperature. Thus in the case of *n*- and *iso*-pentane, when equal weights were heated separately in the same bulb, the *C.I.T.*'s were: Pentane, 253°; *iso*pentane, 260°.

In this experiment the *n*-pentane is less stable than its isomeride, and if there is a relationship between this temperature and spontaneous ignition and detonation, then pentane should detonate more readily in the engine. It has been shown that an *iso*octane possesses

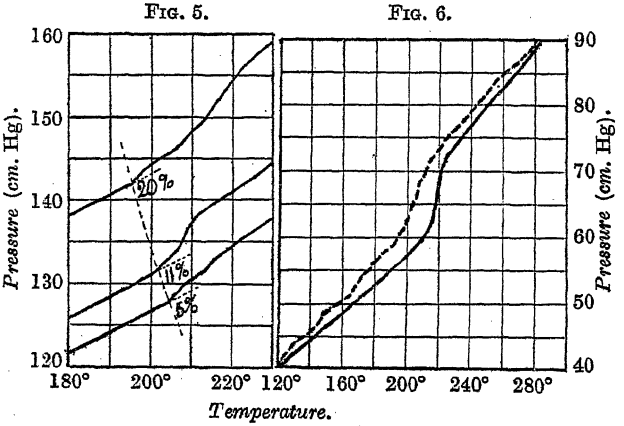
much feebler detonating properties than *n*-octane (Graham Edgar, *Ind. Eng. Chem.*, 1927, **19**, 145).

Surface Area.—The bulbs used were of good soda glass; the effect of surface area is shown by the *C.I.T.* in the following results :

Hydrocarbon.	Large bulb.	Small bulb.
*iso*Pentane	259—260°	263—264°
Heptane	210—212	214—215

Catalysts.—Two typical catalysts were used : (*a*) platinum, an oxidising catalyst, and (*b*) lead tetraethyl, a poison or negative catalyst.

Fig. 5. Fig. 6.



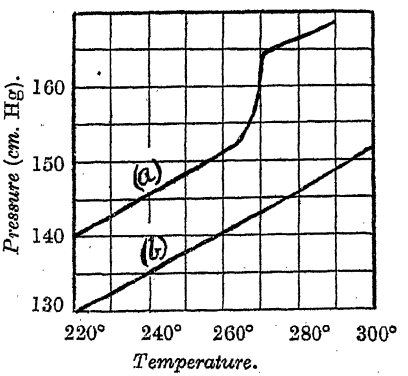
——— *Heptane alone.*

— — — *Heptane with platinum as catalyst.*

(*a*) *Platinum.* This was used both in the form of a coating on the bulb and as platinised asbestos. The effects were very marked : chemical reaction proceeded slowly even at low temperatures, and the pressure–temperature curves showed much irregularity. A typical example of the curves is found in Fig. 6, for heptane, both with and without the catalyst. When the catalyst is present there is a steady rise in pressure above the normal curve, commencing at about 130—140°. Chemical action must be proceeding at or below this temperature. Heating was continued up to 275°; here an unexpected change took place, which must be regarded as a kind of rapid combustion, not an explosion or detonation. The mercury was pushed down the capillary tube with considerable speed, and when it was brought back to zero by raising the manometer, a big increase of pressure was registered. Thereafter, the curve proceeded normally. At the end of the experiment, the bulb was coated with a carbon deposit, and the remaining gases contained carbon monoxide and dioxide. There was none of the usual peculiar smell after heating in the bulbs nor any gummy residue.

(*b*) *Lead tetraethyl.* The remarkable inhibiting properties of this substance were very evident: in every case examined, it either completely obliterated the inflexion in the pressure–temperature curve, or, if a rise did occur when smaller quantities were used, this took place at higher temperatures but was exceedingly small, denoting only slight chemical change with increase in number of molecules. The effect of lead tetraethyl, therefore, is to prevent or reduce that particular chemical change which occurs at the *C.I.T.* A typical example illustrating this fact is given in Fig. 7 for *iso*-pentane, which normally gives a well-defined and easily observed rise of pressure at the *C.I.T.*, but in the presence of 1% of lead tetraethyl there is no sign of a break in the curve up to the highest temperature studied, *viz.*, 298°. On cooling the tube, no gum formation was obtained and the characteristic odour of the oxidation products was absent. In some cases, the bulb was cooled and reheated, and the second curve was then generally in close agreement with the first.

FIG. 7.



(a) iso*Pentane without lead tetraethyl.*
(b) „ *with* „ „

The inhibiting action of lead tetraethyl in oxidation appears to be more general, as the following examples show. The gumming of cracked spirit is attributed chiefly to the formation of peroxides by the "dienes" present. More than a year ago, two samples of cracked spirit were enclosed in glass cylinders, only one of them containing 1% of lead tetraethyl, and at the present time this remains clear and colourless, whilst a thick gum has collected at the bottom of the untreated sample, which is now yellow. These results seem to support Callendar's statement that the action of the lead tetraethyl is to prevent the formation of peroxides. The conditions are, however, entirely different in the two experiments: in the one just described, the temperature is that of the room, and therefore the lead tetraethyl remains as such; at high temperatures it is decomposed, and any negative action must be exerted by the lead itself.

A second experiment was carried out with equal volumes of a light lubricating oil contained in four separate flasks. No. 1 flask was heated to 250° with constant stirring, and then cooled. It had darkened rapidly and become almost opaque. No. 2 contained

lead tetraethyl and during the same treatment underwent little change except in colour (from light yellow to a light reddish tint), but was otherwise quite transparent. The oils in Nos. 3 and 4 flasks, of which only the former contained lead tetraethyl, were exposed to sunlight for some weeks. The latter darkened gradually, and the final appearances of these samples were identical with those of Nos. 1 and 2, which had been heated. In all cases a solid was deposited after several months' standing.

Further evidence of the negative catalytic action of lead tetraethyl is given by dynamic oxidation tests. Air (free from carbon dioxide) was passed through the oil heated to a known constant temperature, then through a series of U-tubes, two empty for collecting light oily products and part of the water, two filled with calcium chloride, and one with soda lime for carbon dioxide estimation. Experiments were carried out (i) heating the oil alone without air bubbling through, (ii) passing air through the heated pure oil, (iii) passing air through the heated oil containing 1% of lead tetraethyl. The weights of carbon dioxide and water produced were determined, and the oil after treatment was examined quantitatively for hard asphalt, coking test (R.A.F.), and acidity. The first experiment was carried out at 200° for 12 hours, and the rate of air flow was 15 litres per hour. The untreated oil darkened very rapidly, becoming almost black, whereas the sample containing lead tetraethyl remained pale yellow for more than 3 hours, after which it darkened slowly, showing that the catalyst was gradually losing its effectiveness. The coking tests, etc., indicated that the treatment was too severe for this oil; the experiments were therefore repeated at 180° with an air-flow of 10 litres per hour, and were stopped at intervals of 2 hours for analysis of the oil and for the weighing of the water and carbon dioxide. These results are in Table IV, and two points are brought out clearly, *viz.*, the inhibiting action of lead tetraethyl (which, however, decreases slowly), and, secondly, the fact that water is produced during oxidation, but is partially suppressed by the lead tetraethyl. This second point seems to favour the theory of primary dehydrogenation, to be discussed later.

Moisture.—When hydrocarbon–air mixtures were heated with appreciable quantities of water, the pressure–temperature curves were peculiar in that they were exceedingly irregular, even for temperatures just above the boiling point of water, and appreciably higher than the normal curve. Apparently water exerted some chemical or catalytic action, and it was decided to try the effect of eliminating moisture. Accordingly, the bulb was dried as far as possible by heating it in a current of dry air; it was then filled with

TABLE IV.

Changes in a light spindle oil due to oxidation.

Conditions of test.	Viscosity * (secs.).	Coking test (mg. per 100 g. of oil).	Hard asphalt, %.	Acidity (mg. per 100 g. of oil).	H_2O evolved, %.	CO_2 %.
(*a*) Original oil	214	0·34	Nil.	9	—	—
(*b*) Heated at 200° for 12 hrs.	261	0·60	Negl.	14	—	—
(*c*) Heated at 200° for 12 hrs., and air passed through at 15 litres per hr. ...	520	2·63	3·96	97	6·37	0·556
(*d*) As in (*c*) but 1% of $PbEt_4$ added	370	2·02	0·44	47	3·41	0·397
(*e*) Heated to 180°; air passed through at 10 litres per hr. for 2 hrs.	245	0·88	—	13	2·34	0·114
(*f*) As (*e*) for 4 hrs.....	353	1·87	—	21	4·20	0·220
(*g*) As (*e*) for 6 hrs. ...	437	2·00	—	49	5·18	0·297
(*h*) As (*e*) + 1% $PbEt_4$	218	0·38	—	9	0·14	0·016
(*i*) As (*f*) + 1% $PbEt_4$	238	0·50	—	13	0·29	0·049
(*j*) As (*g*) + 1% $PbEt_4$	265	0·68	—	19	0·99	0·099

* Determined at 70° F. in a No. 1 Redwood viscometer.

dry oxygen, and hexane was introduced. To the neck of the bulb was attached a tube containing phosphorus pentoxide, and the apparatus was fitted up and allowed to remain for 2 weeks, after which the pentoxide tube was sealed off and a reading taken. It was found that up to 275° there was only a very small rise of pressure above the normal curve, equal to about 10% of that usually occurring.

Contents of Bulb after Heating.—Qualitative tests only have been carried out, and in view of the work recently published by Callendar (*loc. cit.*), the project of quantitative work was abandoned. After being cooled, the contents of the bulbs possessed a peculiar penetrating smell, somewhat resembling that of a terpene. Water (even at temperatures just above the *C.I.T.*), aldehydes, acids, and oxides of carbon were detected, but no peroxides. In the case of all paraffins, however, a certain amount of gum was formed, light yellow for moderate temperatures, black for high temperatures. It was necessary to ascertain if these gums were produced during the process of heating, or if they were formed on cooling. Two test-tubes containing small quantities of octane were heated in a glycerol-bath to 250°, one tube being completely immersed, and the other partially. A brownish gum was observed on the exposed, and hence, cooler, part of the latter tube, whilst the other tube was clear when removed from the bath, but on subsequent cooling the condensed liquid was of a pale yellow colour. It is assumed that

the gums are condensation products of the aldehydes which have been produced at the higher temperatures. Further, when any bulb containing paraffin hydrocarbon is heated above the *C.I.T.* and cooled, there is a fall of pressure, and after reheating, the derived pressure–temperature curve is lower than the first.

Comparative Results for Paraffin Hydrocarbons.—Since the temperature at which initial oxidation occurs is dependent on various factors, a series of experiments was arranged so that conditions were more comparable, and the following details were taken into consideration: (1) The bulbs were of the same material and volume; (2) the rates of heating were identical as far as possible; and (3) the hydrocarbon vapours were in equimolecular proportion.

In Table V are the *C.I.T.*'s of several hydrocarbons of the paraffin series determined under these constant conditions, and also other data appertaining to them. An unsuccessful attempt has been made to discover some physicochemical significance of this initial oxidation temperature, but graphical methods show no linear relationship between these temperatures and boiling point, spontaneous-ignition temperature, heat of formation, or flash-point. The following conclusions, however, are drawn from these figures:

(i) The *C.I.T.* is lowered by increase of molecular weight.

(ii) The temperature for normal hydrocarbons may be below that of the isomerides.

(iii) There is a general parallelism between the *C.I.T.*'s and spontaneous-ignition temperature, both decreasing with rise of molecular weight.

(iv) The flash-point is lowered, whilst the *C.I.T.* is raised, when the molecular weight decreases.

TABLE V.

Hydrocarbon.	Mol. wt.	B. p.	*C.I.T.*	Spontaneous-ignition temp. in oxygen.
n-Pentane	72	36°	255°	476° (560—570° in air).
*iso*Pentane	72	28	263	—
n-Hexane	86	69	230	285°, 288°.
n-Heptane	100	97·5	209	298° (impure), 281°.
n-Octane	114	125	197	—
Nonane (impure)	128	150	193	—

The Mechanism of the Reaction and its Bearing on Detonation.

Two theories have been advanced to explain the primary action of oxidation of paraffin hydrocarbons: the older hydroxyl theory of Bone, and the recently advocated "peroxide" theory of Callendar (*vide supra*). The latter theory possesses no advantage over the former, and differs from it merely in postulating the interposition of two oxygen atoms in place of one between a C–H or C–C linkage. It is true that peroxides have been detected by passing vapour–air

mixture through heated tubes and suddenly cooling the products, the effective yield being increased when the experiment was carried out with droplets, but the experiments of Callendar are inconclusive in that they do not show definitely that the peroxides are alkyl or dialkyl peroxides and not hydrogen peroxide. Even if the former are present they may be the result of secondary oxidation of unsaturated hydrocarbons previously produced, for these substances have been proved to yield peroxides readily. Moreover, there is the difficulty that the volume (or number of molecules) increases at the temperature of initial oxidation to the extent of 15—20% of the number of hydrocarbon molecules present. Peroxide formation can only occur with decrease in the number of molecules, and a simple peroxide decomposition cannot increase the final number of molecules. The pressure–temperature curves given on p. 1559 indicate a sharp rise in the number of molecules at the *C.I.T.*, followed by a small decrease in pressure below the normal curve, indicating chemical change occurring with decrease in the number of molecules.

Stability of Paraffin Hydrocarbons.—This depends on the molecular weight and configuration of the molecule. In accordance with the researches of Berthelot, the effect of heat may be summarised in the reversible reactions

(i) $C_nH_{2n+2} \rightleftarrows C_nH_{2n} + H_2$ (lower temperatures).
(ii) $C_nH_{2n+2} \rightleftarrows C_{n/2}H_n + C_{n/2}H_{n+2}$ (higher temperatures).

Many objections have been raised against this theory of a state of equilibrium, and in actual practice several side reactions may be concurrent, especially at higher temperatures. At 300—400°, however, there is an undoubted production of hydrogen, but this is always accompanied by molecular changes.

A priori reasoning might lead one to conclude that with increasing hydrogen–carbon ratio the former element would split off more easily. Such, however, is not the case, and methane, with its higher proportion of hydrogen, is more stable than any member of the series. For hydrocarbons of this series, the heat of formation may be taken as a measure of the mean stability of the carbon atoms in the molecule. The molecular heat of formation increases with the number of carbon atoms present, but the heat of formation per carbon atom diminishes as shown by Thomsen's results :

Hydrocarbon.	Heat of formation (constant volume).	Mean heat of formation per carbon atom.
Methane (CH_4)	+16·5 Cals.	16·5 Cals.
Ethane (C_2H_6)	22·1	11·05
Propane (C_3H_8)	25·4	8·46
Butane (C_4H_{10})	29·1	7·27
Pentane (C_5H_{12})	1·5	6·30

The same investigator has shown that the average thermal values of the C–C and C–H linkages are approximately the same, so that Mean heat of formation/Valency of carbon may be taken as a relative measure of each valency attraction. There is no experimental justification for assuming that in a given molecule the forces of attraction of the C–C and C–H linkages are equal, and evidence is in favour of the view that there are some hydrogen atoms which are more easily split off than others. Besides the position of the hydrogen atoms and molecular weight, isomerism will be a contributing factor to the ease or otherwise of splitting off the hydrogen atoms.

A comparison of hydrocarbons of the different series presents more difficulty in that the naphthenes and aromatics contain ring compounds, but for those members containing the same number of carbon atoms, *viz.*, hexane, *cyclo*hexane, and benzene, the proportion of hydrogen and heat of formation decrease in the order given, whilst it seems probable, from the scanty data available, that the ease with which hydrogen is split off is greatest for that molecule containing the highest ratio of hydrogen atoms to carbon atoms, the latter being constant in each series.

Primary Dehydrogenation Theory.—The view held, as the result of the experimental work, is that primary oxidation consists in the direct combination of oxygen with those atoms of hydrogen which are most easily split off from the hydrocarbon molecule, the initial products being unsaturated hydrocarbons, containing one or more double bonds, and water. This will account for (*a*) the increase in the number of molecules at the *C.I.T.*, *e.g.*, $2C_2H_6 + O_2 \longrightarrow 2C_2H_4 + 2H_2O$; (*b*) the high percentage of water in the products formed above the *C.I.T.*, this percentage being only slightly increased at considerably higher temperatures; and (*c*) the appreciable proportion of unsaturated hydrocarbons formed near the *C.I.T.*

Secondary reactions ensue, the oxygen combining with the unsaturated hydrocarbons to produce aldehydes, peroxides, etc. This reaction reveals itself in the slight fall in the pressure–temperature curves just above the *C.I.T.* Striking confirmation of this was obtained by heating amylene–air as in the above experiments : an actual depression in the curve occurred, commencing at 232° and continuing up to 254°, after which a gradual rise above the theoretical curve followed. No water was detected in the finally cooled products; but considerable gum formation had taken place.

From the foregoing statements on stability it would appear that methane is the most stable of the hydrocarbons towards oxygen. This is actually the case and it must be observed that the difficulty of oxidation is increased by the probability that two hydrogen

atoms must be removed from one carbon atom to form water, leaving CH_2 residues, which react eventually in various ways. Ethane is far less stable and one hydrogen atom may be removed from each of two adjacent carbon atoms to yield a double bond. Similarly, the higher hydrocarbons can give rise to conjugated double bonds which will enter vigorously into secondary oxidations. In the two cases which have been studied, the normal hydrocarbons appear to be more active than the isomerides. If this statement is of general validity, it may be that the isomeride with the fewest carbon atoms in the main chain is most stable, or that side chains retard removal of hydrogen atoms, or that two or more hydrogen atoms attached to adjacent carbon atoms are more readily oxidised.

Thermal Value of the Dehydrogenation.—The removal of hydrogen with formation of water will be exothermic, and the elimination of only two hydrogen atoms from heptane will produce considerable heat :

$$C_7H_{16} + O = C_7H_{14} + H_2O + 38 \text{ Cals.}$$

These two factors, *viz.*, (*a*) increase in number of molecules, and (*b*) production of heat, must play a considerable part in the detonation of hydrocarbons in petrol engines. The former increases the maximum pressure attained slightly above that calculated from the compression ratio, whilst the second factor may under suitable conditions raise the temperature above that of spontaneous ignition, thus giving rise to pre-ignition. During the slow heating of these hydrocarbon–air or oxygen mixtures, the heat of the initial reactions is dissipated by conduction and radiation, and it has been shown (Callendar) that under such conditions the mixture can be heated to temperatures above 650° without explosion. This is not the case, however, for sudden heating by compression, and, on the assumption that this takes place adiabatically, the theoretical rise in temperature above that resulting from compression alone may be calculated. For a 10% heptane–air mixture, if only two hydrogen atoms are removed from the molecule to produce water, and if the high value of 0·5 cal. is taken as the specific heat of heptane (liquid), the rise in temperature due to primary dehydrogenation alone is calculated to be more than 400°. A final temperature of about 370° is obtained by a compression ratio of 3 : 1, so a theoretical maximum of at least 770° is possible. The high value for the specific heat of heptane is used because it has been shown that condensation of these vapours can occur during compression.

This factor must be considered in the question of detonation. In internal combustion engines, to the heat of compression must be added the heat liberated by primary dehydrogenation, which must

considerably raise both the pressure and the temperature of the mass of vapours. The increase in the number of molecules above the *C.I.T.* will also contribute to a rise in pressure. Primary dehydrogenation must then be the main cause of pre-ignition and detonation, and the ease of detonation increases with the hydrogen ratio. It is significant that the unsaturated hydrocarbons are more unstable and possess lower ignition temperatures than the paraffins, yet the latter detonate more easily. The reason is that the temperatures attained by equal compressions are far from comparable. Any factors, therefore, which will reduce the amount of heat liberated by primary dehydrogenation will diminish the tendency to detonation and allow of higher compressions. They may include reduction of paraffins, especially those of high molecular weight, dilution, negative catalysts, or a preliminary slow heating to a temperature above the *C.I.T.* Moreover, at higher speeds of the engine, the time may be too small to allow of completion of the chemical reactions involved at the *C.I.T.*

Action of Metallic Catalysts.—These are divided into two groups : (*a*) promoters of detonation; (*b*) " antiknocks." They have been classified also as positive and negative catalysts, and there is some apparent connexion between the ease of oxidation and oxide stability, and their catalytic action. The antiknock metals promote the combination of hydrogen and unsaturated hydrocarbons at low temperatures, and it is now suggested that their action as antiknocks depends upon the complete or partial prevention of dehydrogenation with its attendant water and heat formation, thus reducing the final temperature at the end of the compression stroke. From what has been said, it may be concluded that positive catalysts, *e.g.*, platinum, promote the reaction $H_2 + O \longrightarrow H_2O$, and that lead tetraethyl inhibits this change or even poisons the direct action of oxygen on the hydrocarbon, but there is no doubt that the amount of water formed is either nil or almost negligible.

The Action of Unsaturated Hydrocarbons and Aromatics.—These hydrocarbons have an appreciable effect in lowering the detonating qualities of a petrol, but large percentages must be present. It is well known, for example, that " cracked spirit " can be subjected to higher compression ratios than straight spirit, and this raises an objection to the peroxide theory of Callendar. Cracked spirit contains unsaturated hydrocarbons of the olefin type and also dienes even after refining; these are essentially peroxide-forming, and should increase rather than decrease detonation. It is suggested, therefore, that these hydrocarbons are effective as antiknocks in that they (*a*) have a smaller hydrogen content and are less likely to be dehydrogenated, *i.e.*, they act partially as diluents; and (*b*) they

may enter into combination with the hydrogen evolved from the paraffins, by increasing the active mass of unsaturated hydrocarbons. Thus in the reaction $C_nH_{2n+2} \rightleftarrows C_nH_{2n} + H_2$, the olefins produced are reinforced by the unsaturated hydrocarbons of the petrol, and even of the aromatics, and so tend to reverse the reaction with a decrease in the active mass of hydrogen. These unsaturated hydrocarbons are reducing agents. Benzene itself has a tendency to combine with hydrogen at low temperatures. In view of the nature of unsaturated hydrocarbons, their instability, and their tendency to form peroxides, their behaviour in an engine is contrary to expectation; the above may be the real explanation of the facts, and perhaps secondary oxidation products, such as aldehydes, peroxides, etc., are practically negligible on account of the time factor.

The Action of Aromatic Amines.—Any substance that combines with hydrogen under conditions prevailing in the engine, *i.e.*, that competes with oxygen for the hydrogen split off from the hydrocarbons, will tend to decrease detonation. The action of substances such as aromatic amines may be due in small part to dilution, but chiefly to the fact that they undergo decomposition, leaving residues which can unite with hydrogen. In the simplest case, aniline, the possible changes are

$$\text{(i)}\ C_6H_5{\cdot}NH_2 = C_6H_5{\cdot} + {\cdot}NH_2,$$
$$\text{(ii)}\ C_6H_5{\cdot} + {\cdot}NH_2 + 2H = C_6H_6 + NH_3.$$

The effectiveness of such reagents will therefore depend on (*a*) their concentration, (*b*) the ease (or temperature) of decomposition, and (*c*) the thermal action with hydrogen, which should be as small as possible and preferably endothermic.

The action of iodine is capable of some similar explanation, and it is noteworthy that, unlike iodine, bromine and chlorine are slight "knock" inducers; moreover, it is suggestive that their compounds with hydrogen are exothermic, whereas hydrogen iodide is endothermic. Finally, there is the suggestion contained in the above that the ethyl groups from the decomposition of lead tetraethyl increase its efficiency by reducing the effective mass of hydrogen.

Ignition of the Liquid Phase.—The published results of ignition temperatures are far from concordant even when determined by similar methods, and the two factors already discussed, *viz.*, increase of volume at the *C.I.T.* and the exothermic nature of this change, must be considered in methods based upon compression. Moore's method (*J. Soc. Chem. Ind.*, 1917, **36**, 109) consists in allowing drops of the liquid to fall on a hot platinum dish containing oxygen. The liquid phase, however, is less stable than the vapour (see above),

and the results are lower than those obtained by the compression method. Doubtless, too, the size of the droplet and the catalytic effect of the surface play an important part, and this subject is reserved for a future paper. It might be argued that the ignition point of the liquid phase is lower on account of the adsorption of peroxides by the liquid, according to the views of Callendar, but it is known that peroxides do not affect the ignition temperature to any appreciable extent. This constitutes a serious objection to the peroxide theory. According to the views elaborated in this paper, the greater instability of paraffin droplets is due to the great concentration of molecules in the neighbourhood of the drop, with the attendant increase of chemical activity near the surface, and to the fact that the liquid phase absorbs far more heat than the vapour. Thus some of the heat of primary dehydrogenation may be used in suddenly heating the hydrocarbon above its ignition temperature.

ROYAL NAVAL COLLEGE,
GREENWICH, S.E. 10.

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CCVII.—*Striated Photographic Records of Explosion-Waves.*

By COLIN CAMPBELL and DONALD WHITLEY WOODHEAD.

IN a previous paper (J., 1926, 3010) attention was directed to the notable appearance of a moving-film record of the explosion-wave passing through the mixture $2CO + O_2$. Fig. 11 in that paper is remarkable in that closely striated illumination is recorded behind the trace of the wave-front, and not the uniform illumination which occurs in the great majority of previously published photographic records of explosion-waves. Close examination of some of Dixon's records (*Phil. Trans.*, 1903, *A*, **200**, 315; notably Fig. 11, $2CO + O_2$, and Fig. 21, $CS_2 + 2O_2$) discloses striations similar to those now described, but they are ill-defined and do not appear to have been noticed hitherto. The present paper deals with experiments made with a view to define some of the conditions required for the production of such striated records.

The explosive mixture under observation (moist $2CO + O_2$, unless otherwise stated) was contained in a horizontal glass tube 2—3 m. long, usually 15 mm. in internal diameter and 2·5—3·0 mm. in thickness of wall, open at the far end. The flame in this mixture was initiated by the explosion of a hydrogen–oxygen mixture contained in a similar tube in a co-axial position, complete separation of the two mixtures until a very short time before firing being



FIG. 1.

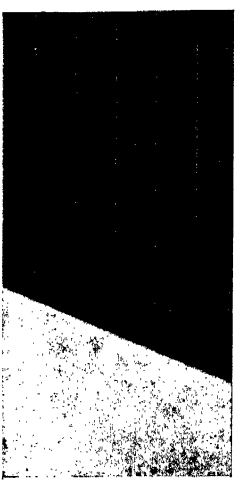


FIG. 2.

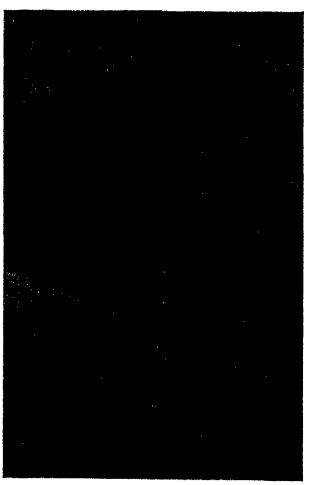


FIG. 3.

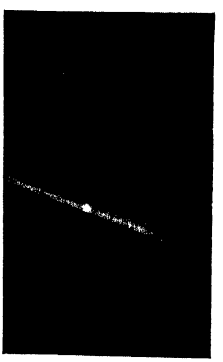
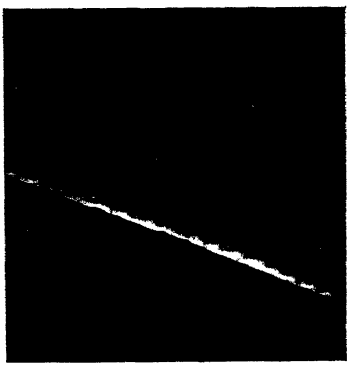


FIG. 4.

Vertical reference lines at intervals of 10 *cm.*

[*To face p.* 1572.]



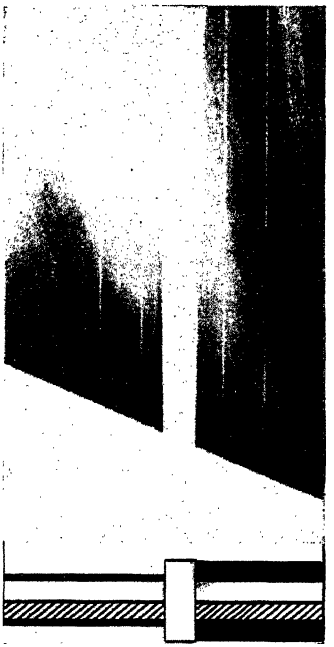


FIG. 6.

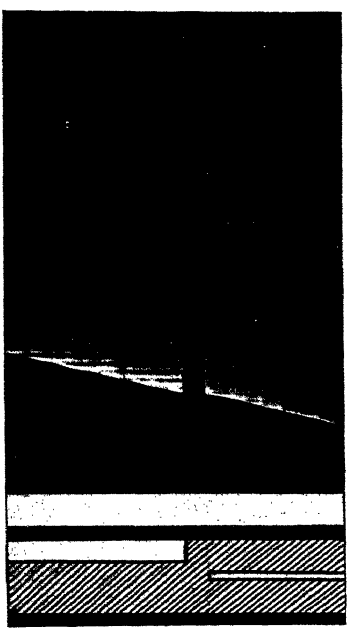


FIG. 9.



FIG. 10.

FIG. 8

at interv 0 cm.

FIG.

[To face p. 1572.]

effected by a metal shutter. The flame was photographed by means of a drum-camera having a peripheral speed of about 45 m./sec. Details of the experimental arrangements are given in our former paper (*loc. cit.*).

The first striated record we obtained was given by the flame in the mixture $2CO + O_2$ to which about 2% of hydrogen had been added (Fig. 1). The mixture was fired by the flame produced by detonating the mixture $2H_2 + O_2$. The flame edge in this record presents a regular undulatory appearance, but the mean rate of progress of the wave is uniform and characteristic of the explosion-wave in this mixture (about 1770 m./sec.). The *apparent* propagation is *per saltum*, each spurt taking place at approximately equal intervals of 45 mm. in the tube, the frequency of the undulations in this record being thus of the order of 39,000 per second. The major portion of the luminosity behind the wave-front is segregated into bands, each of which appears to have its origin in one of the undulations of the wave-front. The bands appear to be equally spaced; they are straight in this record, but definitely curved in others. They are inclined at a small angle to the horizontal in a direction opposite to that of the movement of the explosion-wave, suggesting a reverse motion at some tens of thousands of metres per second. The very high value of this rate is not favourable to the simple interpretation of the bands as a series of waves sent back from the front of the explosion-wave through the burning gases. Moreover, in some records the bands are horizontal, and in two they actually slope forward.

Mode of Ignition.—The production of striated records from $2CO + O_2$ was independent of the means taken to establish the explosion-wave, for they were obtained in equal intensity and with a similar period when the method of ignition was by the explosion-waves from (i) mixtures of hydrogen and oxygen other than $2H_2 + O_2$; (ii) from $C_2N_2 + O_2$; (iii) from $2H_2 + O_2$, which had itself been ignited by a uni-directional spark; or by (iv) direct sparking of $2CO + O_2$ containing about 2% of hydrogen. (Without the presence of a little hydrogen, we failed to obtain the explosion-wave in moist $2CO + O_2$ by direct sparking in a tube 12·5 mm. in diameter and 8 m. long.) In each of these experiments, the photographic record was taken after the explosion-wave had been established. We were unable to detect any differences in records made in similar experiments on Kodak orthochromatic film and on Lumière paper. Figs. 2, 3, 6, and 8 are copies of the negatives obtained with Lumière paper; the remainder are prints made from Kodak films.

Composition of Gases.—When increasing quantities of carbon

monoxide in the mixture $2CO + O_2$ were replaced by hydrogen, the striations remained distinct until the mixture contained about 3% of hydrogen; as the hydrogen content was increased up to about 6%, they became rapidly less distinct; and they were no longer visible when between 6 and 20% was present. Figs. 2, 3, and 4 show this gradation of appearance with 2·2, 3·6, and 10%, respectively, of hydrogen. The compositions of the mixtures are recorded in Table I.

TABLE I.

Mixtures saturated with water vapour at 15°.

Fig.	CO.	O_2.	H_2.	Appearance of record.
	100	50	0	Striated.
1	98	50	2·	,,
2	96·7	50	3·3	Faintly striated.
3	94·6	50	5·4	,, ,,
	91	50	9	Not striated.
4	85	50	15	,, ,,

The distance between successive undulations in the wave-front may be dependent to some extent on the amount of added hydrogen, but this cannot yet be stated with certainty since, as will be shown later, the distance is dependent on the internal diameter of the experimental tube, and differences in the measured distances may be due to slight indeterminate variations in the bores of the glass tubes used.

The presence of hydrogen in a carbon monoxide–oxygen mixture is not essential for the production of a striated record, for such records were obtained of the wave in the mixture $2CO + O_2$, not only when it was saturated with water vapour at room temperature, but also when fairly well dried with sulphuric acid.

The addition of diluent gases (carbon monoxide, nitrogen, and oxygen) to $2CO + O_2$ did not produce any change in the appearance of the records, striations being obtained in each experiment with the mixtures $3CO + O_2$, $4CO + O_2$, $CO + O_2$, and $2CO + O_2 + N_2$. The distance between successive undulations in the wave-fronts did not vary substantially from 45 mm. when the tube was of 15 mm. internal diameter.

Some experiments were made with $2H_2 + O_2$ in which small amounts of the hydrogen had been replaced by carbon monoxide, but no striated records were obtained. Mixtures of hydrogen and oxygen varying in composition from $6H_2 + O_2$ to $2H_2 + 3O_2$ also failed to give striated records. In order to increase the actinic value of the flame in the more dilute mixtures of these gases, the experimental tube was dusted with thorium oxide, and under these conditions very faint striations were obtained only with mixtures containing a large excess of oxygen.

The explosion-wave in certain mixtures of oxygen with methane, ethane, ethylene, carbon disulphide, and cyanogen also gave striated records similar to that reproduced in Fig. 1.

Initial Pressure.—A number of experiments were made with $2CO + O_2$ at initial pressures greater than atmospheric, the experimental conditions being the same as before, save that the far end of the tube was closed. The compression apparatus described by Ellis (J., 1923, **123**, 1435) was used. Striated records were given in all experiments, and the distances between successive undulations were not materially different from those obtained at atmospheric pressure, being 46 and 45 mm. when the initial pressures were 2 and 3 atm., respectively. Fig. 5 is the record obtained at 2 atm. The narrowness of the exposed strip of film is due to the very rapid shattering of the explosion tube after the passage of the wave.

Diameter of Tube.—When explosion tubes of internal diameters less than 15 mm. were used, the records bore striations similar to those obtained with the 15 mm. tubes, but the undulations in the traces of the wave-fronts were nearer together. The striations were thus more closely packed and less easily resolvable. Tubes having internal diameters of 12·5 and 10 mm. were used. The lengths of the undulations, constant in each record, are given in Table II.

TABLE II.

$2CO + O_2$ *saturated with water vapour at* 15°.

Bore of tube, D (mm.).	Distance between undulations, L (mm.).	Ratio L/D.
15	45	3·0
12·5	36	2·9
10	29	2·9

It appears that, within the limits examined, the distance between the undulations is closely related to the bore of the experimental tube. Since the velocity of an explosion-wave is normally unaffected by the diameter of the tube through which it passes, the frequency of the undulations is also related to the bore.

Fig. 6 is a record of the explosion-wave in $2CO + O_2$ contained in an 8 mm. tube; it shows undulations in the wave-front 25 mm. apart ($L/D = 3·0$), with striations lying closely together in the burning gases behind. An additional variant made in this experiment was in the thickness of the walls of the tube. The tube was composite, consisting of two portions cemented together in a metal sleeve (represented on the record by the broad vertical band). The internal diameter was constant throughout, but the thickness of wall changed at the junction from 4 mm. to 1·5 mm. No difference in the characteristic undulations of the trace of the wave-front

in the two portions can be detected. In the diagrammatic representation of the tube given in Fig. 6 (and in succeeding figures) the unshaded area indicates the position of the window in the paper covering of the tube, the solid areas representing the thickness of the tube wall; the diameters are not to scale.

Fig. 7 shows the explosion-wave passing from a 15 mm. into a 9 mm. tube. The two portions of this experimental tube were fused together, and the change in diameter at the junction was made as abrupt as possible. The velocity of the explosion-wave is unaltered by the change in diameter of the tube (see Campbell, J., 1922, **121**, 2483), but the spacing of the undulations is decreased immediately on the entry of the wave into the narrower tube. In the latter, $L = 28$ mm., whence $L/D = 3{\cdot}1$. The tube was intact after the experiment. The striations in the narrow portion of the tube do not appear to exist entirely independently of those in the wider portion, for near the junction the former are apparently retarded, and more markedly so in the gas some distance behind the wave-front. We have here an explosion-wave displaying undulations of two distinct frequencies simultaneously in different portions of the same tube.

A further interesting observation has been made in records showing both detonation-waves and slow flames accelerating rapidly towards detonation. Whereas the explosion-wave is striated, the earlier flame is comparatively uniform, and the striations are usually sharply confined to that portion of the gas which has detonated. In other words, the burning gases in one portion of a tube may show striations, whilst in another portion of the same tube the illumination is normal.

A few of the slow pre-detonation flames which we have photographed show traces of striations of a period similar to those in the later explosion-wave. Because of their narrow and regular spacing these undulations must be regarded as distinct from those of the "vibratory movement" or of the "uniform movement" that precedes it. The undulations of the latter are well-known features of slow flames and result from the establishment of resonance, the flame-front acquiring an undulatory motion leading to vibrations which vary in amplitude according to the extent of the resonance, and in period according to the length of the tube (Mason and Wheeler, J., 1920, **117**, 36).

Photographic Definition.—In order to avoid fogging of the photographic film by extraneous reflexions, the experimental tube was usually enclosed in a sheath of light-proof paper, the light from the explosion reaching the camera through a horizontal slit cut in this covering. Usually the width of this window was equal to the

internal diameter of the tube. The records already described (with the exception of Fig. 6) were obtained through such a window. Although reduction in the width of the window decreased the intensity of the exposure, the striations did not become more clearly defined. However, enhanced photographic definition was secured when a 4 mm. window was cut near the upper (instead of at the middle) portion of the tube. Fig. 8 was obtained with such an arrangement, the position of the window (viewed horizontally from the camera) being shown diagrammatically in the figure. This record is of further interest in showing how the striations persist in the burning gases for some time after the wave-front has reached the open end of the explosion-tube.

An experiment was arranged in which a central window 2 mm. and an upper window 4 mm. wide were cut in the paper sheath over different lengths of the same tube. The record (Fig. 9) shows the clearly defined striations from the upper window, whilst the exposure from the central window produced a greater number of less well-defined striations. In a further experiment, a lower window 4 mm. wide was made in the second portion of the same tube. The record (Fig. 10) shows that there was in the illumination from each of these windows an independent series of undulations out of phase with one another, their alternate appearances occurring at approximately equal time intervals (about 1/80,000 sec.). Undulations visible through narrow central windows have periods considerably shorter than those recorded when the window is of the same width as the diameter of the tube. A similar, but temporary, effect has been observed through wide windows during the first 20 cm. of travel of the flame in $2CO + O_2$ after its ignition by the flame of $2H_2 + O_2$ (*e.g.*, in Fig. 1), before the flame-speed had completed its fall to that normal for the detonation-wave in $2CO + O_2$.

Summary.

Some of the conditions required for the production of an apparently undulatory form of the explosion-wave have been examined. This form appears to be characteristic of the wave in the mixture $2CO + O_2$ and in some of the more dilute mixtures of carbon monoxide and certain other gases with oxygen or oxygen and nitrogen. The presence of about 6% of hydrogen in $2CO + O_2$, saturated with water vapour at the ordinary temperature, eliminated visible undulations.

Increase in the initial pressure of the gaseous mixtures to 3 atm. did not effect any definite change in the distance between the undulations, but this was found to depend directly on the internal diameter of the explosion-tube. The most sharply defined records

were obtained when only the layers of gas near the walls of the tube were visible to the camera. The undulations visible through a window in the extreme upper portion of a tube occurred alternately with those visible through the extreme lower portion.

The experimental evidence is not yet sufficient to afford a complete interpretation of the striated records. It does not indicate whether they are due to induced vibrations of the apparatus or to a periodic propagation of the explosion-wave. It can be said, however, that the striations are not due to mechanical chattering of the heavier parts of the camera, since undulations of two different periods can be obtained on one and the same record.

An interpretation based on the assumption that the records disclose what is actually occurring in the flames has been communicated to us by Mr. E. F. Greig, who suggests that the part of the wave-front, the light of which affects the photographic film, traverses a helical path on the walls of the tube. The extension of this interpretation to the illumination from the outer layers of the burning gases *behind* the wave-front would also imply a rotation of the source of light affecting the photographic film. It is clear that a wave being propagated along a helical path could account for the dependence of the length of the undulations on the bore of the tube and for the alternate production of undulations in the records from the upper and lower windows. Further experiments are in progress to test the validity of this and the other possible interpretations mentioned above.

We wish to acknowledge our indebtedness to the Chemical Society and the Brunner–Mond Research Fund Committee for grants towards the cost of photographic materials and apparatus, and to Mr. A. C. Finch, B.Sc., for laboratory assistance.

THE UNIVERSITY, MANCHESTER. [*Received, April 14th,* 1927.]

CCVIII.—*The Nature of the Sintering of Active Copper Catalysts.*

By FREDERICK HUBN CONSTABLE.

THE conceptions of Taylor (*Proc. Roy. Soc.*, 1925, *A*, **108**, 106) and of Armstrong and Hilditch (*ibid.*, p. 111) concerning the structure of active metallic surfaces seem to have progressed very far in such a direction as to attribute to the centres of activity a quantity of energy that would approach the heat of vaporisation of the metallic atoms (see Constable, *ibid.*, p. 355). Armstrong and

Hilditch have assumed that the nickel atom responsible for hydrogenation reactions is actually gaseous at the instant of the chemical change. Pease (*J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2238, 2297) and Constable (*Proc. Roy. Soc.*, 1926, *A*, **110**, 283), while fully convinced of the existence of centres of activity, do not attribute to them such great energy, the facts being much more in accord with the assumption that they consist of groups of atoms frozen in such a manner that they can still possess intense fields of external force, while being far removed from the condition of vapour.

Taylor (*loc. cit.*) laid considerable stress on the sensitiveness of the surface to heat treatment: "A granule of the catalyst must therefore possess, in part, the ordered arrangement of the atoms found in crystals of the metal. The sensitivity of the product to even moderate heat treatment, whereby marked sintering occurs, suggests that this completely ordered arrangement of the atoms has not been attained, and that here and there, on the surface of a mainly crystalline granule, there are groups of atoms in which the processes of crystallisation are not yet complete." In reality the process of sintering is more complicated than this,* for the boundaries of individual grains are in contact, and therefore the granular structure is itself capable of such a growth as to reduce the area of the exposed surface in a marked degree. Thus, evidence that heat treatment reduces catalytic activity is valueless by itself as a criterion that some of the active centres on the surface have collapsed owing to the increased thermal agitation, for the total active surface has also been reduced in a marked manner. It is therefore essential for the solution of the problem to measure both the surface area of the catalyst and its catalytic activity.

The investigations of Dunn (*ibid.*, 1926, *A*, **111**, 210) provide a means of elucidating this problem. If the course of oxidation of a metal be followed, both by measurements of the electrical conductivity of the metal–oxide mixture, and by estimation of the thickness of the surface film of oxide by means of its colour in normally reflected light, a direct measure of the surface area of the catalyst can at once be obtained. Unfortunately, it is only possible to estimate the equivalent air thickness of the oxide film, *i.e.*, the thickness of a film of air that would produce the same colour effects, and thus the absolute measurement of the area of the surface is not possible by this method, without introducing very distinct assumptions as to the refractive index and nature of the oxide. It is, however, possible to measure the fractional decrease in the

* There are at least two variables: the number of centres of activity per unit area of the surface, and the relative rate of reaction on each individual centre of activity.

surface area when the catalyst is exposed to a high temperature. Let S be the surface area of the catalyst, C the conductivity of the film of metal supported on a China-clay rod, a the thickness of the oxide film, t the time the metal has been exposed to oxidation, and ρ the density of the oxide of mass W. Then, assuming that the electrical conductivity of the film is a measure of its metallic content (compare Palmer, *Proc. Roy. Soc.*, 1921, *A*, **103**, 444),

$$\rho S(da/dt)/W = -(dC/dt)/C \quad . \quad . \quad . \quad . \quad (1)$$

As the oxidation proceeds, the value of S must become smaller, and as its *initial* value only is important, it is necessary to measure da/dt and dC/dt at the commencement of the reaction. According to Dunn (*loc. cit.*; his conclusions are confirmed by the present work), the process is controlled by the rate of diffusion of oxygen through the protecting layer, and if W is the weight of the oxide formed in time t, then

$$W^2 = Kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K is a constant. It was found that both the fall in the conductivity and the equivalent air thickness follow the law quoted above for the weight of oxide formed in time t, when the catalysts are rendered inactive by sintering. But for the most active catalysts the value of K obtained fell considerably with increasing time. Dunn showed this to be due to the influence of time on the oxide film: some hardening process apparently takes place which causes the film to become less permeable to oxygen. Therefore, in the case of active catalysts it is necessary to find the *initial* value of K in equation (2).

If c be the fall in conductivity, *i.e.*, $c = C_0 - C_t$, then $c^2 = K_c t$. Hence $dc/dt = \frac{1}{2}\sqrt{K_c/t}$; similarly $da/dt = \frac{1}{2}\sqrt{K_a/t}$. Thus equation (1) becomes

$$\rho S\sqrt{K_a}/W = \sqrt{K_c}/C \quad . \quad . \quad . \quad . \quad (3)$$

Let the symbols with suffix 1 relate to the active catalysts, and those with suffix 2 to the sintered catalyst; then dividing the two equations of type (3) for the active and sintered catalysts, respectively, after the same small time interval t from the commencement of the oxidation of each at the same temperature, we obtain

$$S_2\sqrt{K_{a_2}}/S_1\sqrt{K_{a_1}} = \sqrt{K_{c_2}/K_{c_1}} \quad . \quad . \quad . \quad . \quad (4)$$

The ratio of the area of the catalyst in its two states (*i.e.*, S_2/S_1) can thus be measured and compared with the fall in catalytic activity, without assuming any particular value for the refractive index of the copper oxide.

Experimental.

The films used were prepared as described previously (*Proc. Roy. Soc.*, 1924, *A*, **106**, 251). They were rendered active by alternate oxidation and reduction at 210°, and the nature of the departure from the parabolic law was studied, together with the effect of arrested oxidation. The fractional conductivities of the film of copper and the constants of the parabolic law are shown in Table I.

Table I.

t (mins.).	Fraction of original metal remaining.	c (ohm^{-1}).	$c^2/t = K_c$.
0	1·000	0·000	—
1	0·747	0·149	0·0222
2	0·671	0·193	0·0183
3	0·600	0·236	0·0159
4	0·558	0·261	0·0170
5	0·525	0·281	0·0157
6	0·494	0·299	0·0149
10	0·422	0·342	0·0117
15	0·349	0·385	0·0099

The fall in the initial conductivity noticed by Dunn was confirmed, some 18% being lost in five alternate oxidations and reductions. The fractions of the initial conductivities were plotted against time, so that each curve should be strictly comparable. If the arrested oxidation follows the same law, then the value of the constant so obtained would be of importance as a characteristic of the hardened oxide film produced in the second experiment. A difficulty arises in calculating the value of K_c for all curves after the first, because the origin of the later curves is not the point $t = 0$, $c = 1{\cdot}00$; this can be removed by considering later curves as part of a parabolic curve of the form $c^2 = K_c(t + \tau)$, and deriving K_c from the relation $2c.dc/dt = K_c$. The results so obtained are recorded in Table II.

The value of K_c is thus the same whether the oxidation has been arrested for 20 or 70 minutes; hence the sintering and hardening of the oxide is moderately rapid. The oxide formed during continuous oxidation has, however, a higher permeability to oxygen, since it does not have time completely to attain the final state, owing to the constant formation of a fresh layer. The result nevertheless confirms that the fall in the constant for the most active catalysts can be accounted for by the hardening of the newly formed oxide layer; thus it is necessary for the solution of equation (4) to compare the values of K in the initial stages of the oxidation.*

* It is fortunate that the values of K, both for the equivalent air thickness curves and for the fall in conductivity compared with time, fall in the same manner for the most active catalysts. Hence the average values may be used for comparison, and for solution of equation (4).

TABLE II.

The constant in the parabolic law for catalysts whose oxidation has been arrested and then continued.

t.	Fall in conductivity.	Mean c over interval.	Time interval.	Δc.	$K_c \times 10^3$.
		A. Oxidation arrested for 20 mins.			
0	0·000				
2	0·198				
5	0·229	0·233	10 — 2 = 8	0·069	4·00
10	0·267	0·260	15 — 5 = 10	0·063	3·27
15	0·292	0·290	20 — 10 = 10	0·047	2·73
20	0·314				
		B. Oxidation arrested for 70 mins.			
2	0·216				
5	0·254	0·248	10 — 2 = 8	0·064	3·96
10	0·280	0·288	15 — 5 = 10	0·068	3·92
15	0·322	0·310	20 — 10 = 10	0·059	3·76
20	0·339				

The same film of metallic copper was studied by simultaneously measuring its conductivity and comparing its colour with a standard. An activated film, prepared at 210°, was sintered at 440° for 10, 50, 100, and 200 minutes, and its rate of oxidation studied immediately after each sintering. (After each experiment the film was reduced at 210° by carbon monoxide, and sintered for the requisite time for the next experiment.) It was more convenient to use an old rod coated with copper which had been oxidised and reduced a large number of times; there was thus less volatilisation of copper during the series of experiments than would have been found with a freshly prepared rod.

The results obtained with the old rod are recorded in Table III, which shows the validity of the parabolic law; α represents the equivalent air-thickness of the oxide film (in cm. $\times 10^{-5}$), and K_a is the corresponding constant ($K_a = \alpha^2/t$).

The mean values of K_c and K_a are used, since it is evident from Tables III A and B that the fall in the constants for the fully activated catalysts occurs in the results of both methods and to a strictly comparable extent (see footnote, p. 1581). The surface area is reduced to about one-third while the catalytic activity is reduced to about one-seventh; thus the reduction in the surface is somewhat more effective in reducing the catalytic activity than is the collapse in the actual centres existing on the surface.

It has therefore been shown that the active centres collapse when exposed to temperatures considerably in excess of those at which the surface was formed, and hence that these centres of activity are in a state of strain. But the coarse structure seems to collapse even more easily, suggesting that the energy present in the centres

TABLE III.

The oxidation of active and sintered catalysts at 210°.

A. Measurements by the conductivity method.

Time of sintering at 440° (mins.).

	0·0		10		50		100	
t.	*c.*	$100K_c$.	*c.*	$K_c \times 10^3$.	*c.*	$K_c \times 10^3$.	*c.*	$K_c \times 10^4$.
0	0·000	—	0·000	—	0·000	—	0·000	—
1	0·142	2·02	0·086	7·41	0·045	2·01	0·030	9·00
2	0·191	1·82	0·122	7·45	0·066	2·18	0·036	6·48
3	0·234	1·82	0·150	7·50	0·079	2·08	0·048	7·68
4	0·249	1·55	0·171	7·30	0·092	2·12	0·055	7·56
5	0·272	1·48	0·184	6·76	0·103	2·13	0·068	9·23
6	0·287	1·37	0·203	6·86	0·108	1·95	0·071	8·38
7	0·303	1·31	0·225	7·23	0·123	1·80	0·078	8·68
8	0·312	1·22	0·241	7·26	0·134	2·22	0·083	8·61
10	0·338	1·14	0·259	6·71	0·149	2·21	0·101	10·2
12			0·276	6·34	0·162	2·62	0·112	10·4
14			0·299	6·38	0·178	2·63	0·126	11·3
			Mean value of K_c.					
	$1·52 \times 10^{-2}$		$7·02 \times 10^{-3}$		$2·18 \times 10^{-3}$		$8·76 \times 10^{-4}$	

B. Measurements by the colour method.*

Time of sintering at 440° (mins.).

	0·0		10		50		100	
t.	*a.*	$K_a \times 10^{10}$.	*a.*	$K_a \times 10^{10}$.	*a.*	$K_a \times 10^{10}$.	*a.*	$K_a \times 10^{10}$.
0	0·0	—	0·0	—	0·0	—	0·0	—
1	2·0	4·0	1·5	2·2	1·3	1·7	1·2	1·4
2	2·4	2·9	2·1	2·2	1·9	1·8	1·6	1·3
3	2·8	2·6	2·6	2·3	2·2	1·6	2·2	1·6
4	3·1	2·4	3·0	2·3	2·5	1·6	2·3	1·3
5	3·3	2·2	3·2	2·0	2·9	1·7	2·6	1·4
6	3·6	2·2	3·5	2·0	3·0	1·5	2·9	1·4
7	3·9	2·2	3·8	2·1	3·3	1·6	3·2	1·5
8	4·1	2·1	4·0	2·0	3·6	1·6	3·4	1·4
9	4·3	2·0	4·2	2·0	3·9	1·7	3·7	1·5
10							3·9	1·5
			Mean value of K_a.					
	$2·50 \times 10^{-10}$		$2·12 \times 10^{-10}$		$1·63 \times 10^{-10}$		$1·43 \times 10^{-10}$	

* Estimated from Rollett's table (*Sitzungsber. K. Akad. Wien*, 1887, **57**, 229) of the colours of Newton's rings in transmitted light.

TABLE IV.

Comparison of fall in catalytic activity in the dehydrogenation of alcohol with the decrease in surface area.

Time of sintering (mins.)	0·0	10	50	100	200
$K_c \times 10^4$	152	70·2	21·8	8·76	8·19
$K_a \times 10^{10}$	2·50	2·12	1·63	1·43	1·33
Fractional surface area	1·00	0·72	0·468	0·32	0·33
Rate of dehydrogenation observed with six rods similarly prepared	3·21	1·71	0·47	0·43	0·43
Fractional reaction velocity	1·00	0·53	0·146	0·134	0·134
Reaction velocity per unit area of catalyst	1·00	0·74	0·31	0·42	0·40

of activity is not very greatly in excess of that possessed by the regular arrangement of the surface atoms. Thus the theory in the form advanced by Taylor, and by Armstrong and Hilditch, seems to be too drastic, and the more moderate views of Pease and Constable accord better with the experimental facts.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, May 23rd*, 1927.]

CCIX.—*The Electroendosmosis of Aqueous Solutions through a Diaphragm of Sintered Glass Powder.*

By FRED FAIRBROTHER and HAROLD VARLEY.

GLASS capillaries and diaphragms of powdered glass have been used for many quantitative investigations on electrokinetic phenomena. A review of the earlier work (to the end of 1913) is given by Smoluchowski (Graetz, "Handb. d. Elektrizität u. des Magnetismus," Vol. 2, p. 366). Powis (*Z. physikal. Chem.*, 1915, **89**, 91), Kruyt (*Kolloid Z.*, 1918, **22**, 81), Freundlich and Rona (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, **20**, 397), and Hepburn (*Proc. Physical Soc.*, 1926, **38**, 363; 1927, **39**, 99) have also used a glass–water interface for electrokinetic experiments.

The results of Lachs and Kronman (*Bull. International Acad. Polonaise*, 1925, **10**, *A*, 289), however, appear to throw some doubt on the quantitative value of previous work, for they found that the stream potentials through glass and quartz capillaries could be reproduced with an accuracy of only 14% under seemingly identical conditions, and they state that "the streaming potential has no constant value and is varying in time." Hence they argue that all results obtained for flow potentials of aqueous solutions in glass or quartz capillaries must be considered to be merely qualitative (*Rocz. Chem.*, 1926, **6**, 641). Such a conclusion necessarily involves also electroendosmosis of aqueous solutions through glass powder or capillary tubes.

The results now recorded, which were carried out before the work of Lachs and Kronman came to our notice, were the outcome of preliminary experiments with diaphragms of sintered Jena-glass powder, carried out with aqueous solutions prior to the use of such a diaphragm for electroendosmotic investigations in non-aqueous systems.

A diaphragm of sintered glass powder possesses the advantages of rigidity and simplicity, *i.e.*, no foreign material (glass wool, etc.) is required to keep the diaphragm in place, and the apparatus can

be made of the same kind of glass holding the diaphragm fused in position.

EXPERIMENTAL.

The apparatus employed was essentially that described by Fairbrother and Mastin (J., 1924, **125**, 2319), the central compartment A (*loc. cit.*) being replaced by a tube carrying the sintered diaphragm fused into its centre, and the capillary tubes, EE, extended to the sides of the diaphragm. The particular glass disc used, of sintered Jena "Geräte" glass, was of the closest grain manufactured (designated as G3/<7), and was approximately 2 cm. in diameter and 3 mm. thick. It was supplied fused in position by the makers, Messrs. Schott u. Gen. of Jena.

The diaphragm was cleaned first in alcohol or acetone to remove grease, and then in concentrated sulphuric acid. Air was removed from the pores by placing the tube carrying the diaphragm in a larger tube, and evacuating by a water pump; a small quantity of air-free water was then admitted to the containing vessel and allowed to boil under reduced pressure for some time, after which air-free water was allowed to fill the vessel. Before each series of estimations, the apparatus was well rinsed with the solution employed, several hundred c.c. being allowed to pass through the diaphragm over-night.

The value of l/q (the ratio of the effective length of the diaphragm to its effective cross section) was measured with several solutions in the manner described by Fairbrother and Mastin (*loc. cit.*). Each estimation was repeated many times with various voltages across the diaphragm. The individual readings showed good agreement. In Table I are the average values of l/q for each solution; they show a small increase with concentration, even in such comparatively well-conducting solutions.

TABLE I.

Solution.	l/q.	Solution.	l/q.
N/100-KCl	1·723	N/100-HCl	1·758
N/10-KCl	1·736	N/10-HCl	1·782
N/5-KCl	1·751	N/5-HCl	1·783
N/1-KCl	1·755		

In Table II are the results of electroendosmosis experiments with water and dilute hydrochloric acid. ET (in volt-seconds) is the product of the potential gradient across the diaphragm and the time for the transport of 1 c.c. of solution. ζ, the potential of the double layer as calculated from the Helmholtz–Smoluchowski formula, is also given for comparison; in making this calculation, a value for l/q of 1·77 has been assumed.

For some time no great difficulty was experienced in obtaining concordant and reproducible results, which are given as Series I.

TABLE II.

	Series I.		Series II.	
Solution.	*ET*.	ζ (volt).	*ET*.	ζ (volt).
Water	4,520	−0·0557	14,880	−0·0169
N/5000-HCl	4,880	−0·0516	26,700	−0·0094
N/1250-HCl	5,668	−0·0444	43,500	−0·0058
N/400-HCl	6,546	−0·0394	?	0·00
N/100-HCl	10,200	−0·0247	17,970	+0·0140

At this time, the glass was still negatively charged in *N*/40-hydrochloric acid. During experiments with this solution, however, effects similar to those found by Lachs and Kronman were first observed, *i.e.*, ζ became less negative with time. Repetition of the estimations in the solutions previously used gave the results of Series II, the diaphragm having in the meantime been carefully cleaned. The results obtained in this series were also quite concordant among themselves, but ζ was throughout less negative than in the same solution in Series I. The glass surface appears to have undergone some change which has the effect of rendering it more positive. Experiments with dilute solutions of lanthanum nitrate gave further indications that ζ was decreasing with increase of time; and at the conclusion of these experiments, ζ in distilled water was found to have undergone a further decrease.

Some time previous to the foregoing experiments, the permeability of this particular diaphragm had been measured for the purpose of proving that Poiseuille's law held good, and that the resistance of the bubble and connecting tubes to the flow of water was negligible compared with that of the diaphragm—necessary conditions for accurate work by our method. It was found that the diaphragm had a "specific permeability" at 20° of $2{\cdot}10 \times 10^{-4}$: by this term is meant the number of c.c. of water passing through per second under a head of 1 cm. of water. After the foregoing experiments, the permeability was redetermined, and was found to have fallen to $2{\cdot}43 \times 10^{-5}$, or about one-ninth of its former value.

The permeability estimations were carried out by allowing boiled distilled water, under a head of about 80 cm. (measured by a cathetometer), to flow through the diaphragm and escape by a small tube into a tared weighing bottle. The estimations were performed in a room the temperature of which remained practically constant during an estimation. The temperature of the water was further observed in the proximity of the diaphragm, and the permeability corrected for changes in viscosity and density to 20°. Great care was taken to ensure the absence of grease or suspended impurities in the water.

Continued passage of water through the diaphragm brought about a still further decrease of permeability. After the diaphragm had been soaked over-night in pure concentrated nitric acid, the permeability rose to $2{\cdot}038 \times 10^{-4}$, which is approximately the same as that found originally. Subsequent passage of water again effected a decrease in the permeability, rapidly at first, and then more slowly.

It was observed that the permeability decreased at a greater rate if the water were passed through than if it were allowed merely to remain in the diaphragm. A determination of the electroendosmosis in distilled water, immediately after the diaphragm had been treated with nitric acid, gave $\zeta = -0{\cdot}0557$ volt, which is the same as that initially found. This, however, was only a temporary value, and subsequent estimations in dilute hydrochloric acid agreed more nearly with Series II.

The decrease in permeability on passage of water was confirmed with other diaphragms. In one case, where the porous plug was of the same kind as that used above, but 5 mm. instead of 3 mm. thick, even consecutive estimations showed a decrease, and in 4—5 hours the permeability fell from $1{\cdot}746 \times 10^{-5}$ to $0{\cdot}574 \times 10^{-5}$. Another plug of the same porosity, 3 cm. diam. and 3 mm. thick, was attached directly to the receiver of a conductivity-water still: passage of about 3 litres of water, over a period of a week, reduced the permeability to half its initial value.

In these latter cases the change appears to have taken place much more quickly than with the apparently similar filter disc used in the first set of experiments. This may be partly accounted for by the fact that the first disc had been heated and annealed more than the others, during the process of forming ground joints on the tube which contained it. In the case of this diaphragm also, it would almost appear that there was an initial period during which no appreciable change took place.

Discussion.

The foregoing results suggest strongly that the glass surface has undergone a swelling process. Haber and Klemensiewicz (*Z. physikal. Chem.*, 1909, 67, 385) postulate the existence of a swollen layer on the surface of the glass in explaining their observations with the glass electrode, and Lachs and Kronman (*loc. cit.*) suggest that their results are probably due to a swelling process which advances with time.

A simple decrease in the effective size of the pores of the diaphragm, although explaining a decrease in the amount of electroendosmosis, and hence in the (negative) value of the interfacial potential (when this is calculated on the assumption of a too small

value of l/q), would not in itself bring about a reversal in the direction of electroendosmosis. We must therefore conclude, either that the swelling of the surface layer is accompanied by a change which has the effect of imparting a positive charge to the diaphragm, or that the distribution of potential within the swollen layer is such as to cause a reversal of sign in certain solutions, *e.g.*, $N/100$-hydrochloric acid. Lachs and Kronman attribute the decrease of ζ, due to the thickening of the wall layer by swelling, to a shifting of the line along which displacement occurs (Fig. 1, A and B).

If, however, the course of the potential should be as in Fig. 2, as suggested by Freundlich ("Kapillarchemie," 1922, p. 342) in order to explain the difference in sign between thermodynamic and electrokinetic potentials, then we might obtain a reversal of direction of electroendosmosis by a thickening of the wall layer.

FIG. 1.

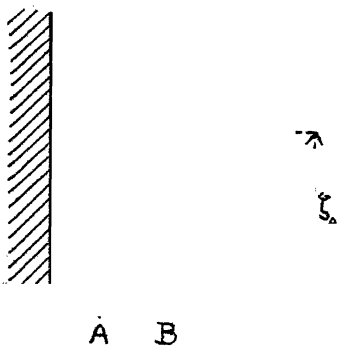
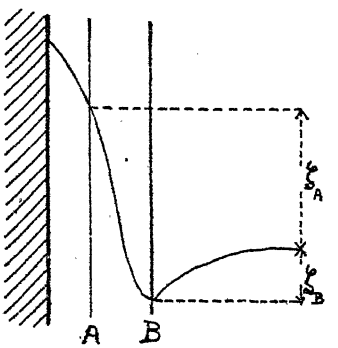


FIG. 2.



The present work therefore supports the conclusion of Lachs and Kronman, that the interfacial equilibrium between glass and aqueous solutions is not a true one, but one which changes with time. Since, however, the change in the surface may, with suitable material, take place relatively slowly, this change does not necessarily invalidate experiments carried out on the effects of ions of different kinds on the interfacial potential. It is to be expected, for example, that the change will occur more slowly with the Jena "Geräte" glass used in the present work than with the ordinary Thuringian glass used by Lachs and Kronman.

We also passed considerable quantities of alcohol and of benzene through the dried diaphragm, without observing any change in the permeability to these liquids. Such a diaphragm, therefore, can probably be used successfully for quantitative experiments in non-aqueous liquids.

Summary.

(1) Electroendosmosis experiments have been carried out with a diaphragm of sintered Jena " Geräte " glass powder in water and in dilute hydrochloric acid.

(2) The amount of electroendosmosis decreased after a time, and in $N/100$-hydrochloric acid it became reversed in direction.

(3) Experiments were also carried out on the permeability of the diaphragm to water. This also decreased with the time during which water was passed through the diaphragm.

(4) It is suggested that these results indicate that the glass surface undergoes a swelling process, and, further, that the distribution of potential within the swollen layer may account for the reversal of direction.

In conclusion, we should like to thank Mr. C. E. Marshall, who carried out a number of preliminary measurements, and to acknowledge our indebtedness to the Chemical Society Research Fund and the Brunner-Mond Research Grant to this Department, which have partly defrayed the cost of this work. One of us (H. V.) also desires to thank the Department of Scientific and Industrial Research for a maintenance grant during its prosecution.

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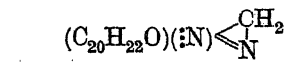
CCX.—*Strychnine and Brucine. Part IV.*

By GEORGE ROGER CLEMO, WILLIAM HENRY PERKIN, junr., and ROBERT ROBINSON.

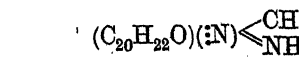
THE present communication contains the description of part of a general investigation into the reduction products of strychnine, $C_{21}H_{22}O_2N_2$, and is mainly concerned with the examination of strychnidine, $C_{21}H_{24}ON_2$. It also includes a short account of experiments which we have carried out on the decomposition of methylstrychnine under various conditions.

Our knowledge of the reduction products of strychnine is due almost entirely to Tafel, who in 1892 (*Annalen*, **268**, 235, 245) published the results of an important investigation on the reduction of this substance with hydriodic acid in the presence of phosphorus. He showed that strychnine, under these conditions, is converted into deoxystrychnine, $C_{21}H_{26}ON_2$, by the addition of six atoms of hydrogen and elimination of water. This important substance yields, on hydrolysis, deoxystrychnic acid, $C_{21}H_{28}O_2N_2$, which, on treatment with acids, is again converted into deoxystrychnine.

It is clear, therefore, that it still contains the group —CO·N=, so characteristic of strychnine, and that it is the second oxygen atom in the molecule which has taken part in the reduction. In a subsequent paper (*Annalen*, 1898, **301**, 285), Tafel describes the reduction of deoxystrychnine (i) to strychnoline, $C_{21}H_{26}N_2$, by treatment with sodium and *iso*amyl alcohol and (ii) to dihydrostrychnoline, $C_{21}H_{28}N_2$, by electrolytic reduction. Tafel also examined the products of the electrolytic reduction of strychnine itself, and showed that this substance is converted, under the conditions he employed, into a mixture of strychnidine, $C_{21}H_{24}ON_2$, and tetrahydrostrychnine, $C_{21}H_{26}O_2N_2$. Since the latter is converted into the former by dehydrating agents, he suggested that the relationship between these substances is probably that represented by the scheme:

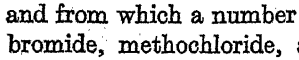


Strychnidine.



Tetrahydrostrychnine.

In the course of an inquiry into the properties of strychnidine, we have much simplified the preparation of this substance and its separation from tetrahydrostrychnine (p. 1600), and we have thus been able to prepare, in a comparatively simple manner, both of these substances in considerable quantities. The results of an investigation into the properties and decompositions of tetrahydrostrychnine, which are of considerable interest, will form the subject of a later communication. The starting point in the experiments described in the present communication has been strychnidine methosulphate, $C_{21}H_{24}ON_2,Me_2SO_4$, which has been obtained (i) by the direct union of strychnidine with methyl sulphate and (ii) from strychnine methosulphate by electrolytic reduction, and from which a number of simple derivatives such as the methobromide, methochloride, and methiodide have been conveniently prepared.

From the fact that these two methods give rise to identical substances, it is evident that the nitrogen atom which is methylated in the course of the formation of strychnidine methosulphate is not that which occurs in the amide group of strychnine. Strychnidine methosulphate is therefore  . When strychnidine methosulphate is digested with methyl-alcoholic potash it is converted into *methoxymethyldihydrostrychnidine*, $C_{23}H_{30}O_2N_2$, m. p. 126°, which crystallises splendidly in prisms, the interesting peculiarities of which have been examined by Dr. T. V. Barker (see p. 1602). This substance, produced from strychnidine by the introduction of a methyl group and addition of methyl

alcohol, is a mono-acid base yielding a *hydriodide*, $C_{23}H_{30}O_2N_2$,HI, and a *methiodide*, $C_{23}H_{30}O_2N_2$,MeI, and the latter is converted by silver hydroxide into the *methohydroxide*, $C_{23}H_{30}O_2N_2$,MeOH, m. p. 117°. Like strychnidine, but unlike strychnine, these substances give each an intense crimson coloration when a drop of dichromate is added to its solution in dilute sulphuric acid, and this and other reactions (see below) suggest that the further methylation of methoxymethyldihydrostrychnidine again occurs at that nitrogen atom which is responsible for the basic properties of strychnine. The conclusion appears inevitable that methoxymethyldihydrostrychnidine and its methiodide should be represented by the expressions

$$C_{20}H_{22}O(OMe)(:NMe)\begin{cases}CH_2\\ \\ N\end{cases} \quad \text{and} \quad C_{20}H_{22}O(OMe)(:NMe_2)\begin{cases}CH_2\\ \\ N\end{cases}\Big\}I$$

respectively.

The simplest conceivable formulation of the decomposition of strychnidine methosulphate by means of methyl-alcoholic potassium hydroxide is in accordance with the scheme:

$$\begin{matrix}>C-NMe\\ \\ >C-N\end{matrix}\Big\}SO_4Me \text{ and } MeO\}K \longrightarrow \begin{matrix}>C(OMe),\\ \\ >C=N\end{matrix}\Big\}Me \text{ and } SO_4Me\}K.$$

It is, however, by no means certain that the groups $C_{20}H_{22}O$ of strychnidine and of methoxymethyldihydrostrychnidine are identical. Indeed the reconstitution of the quaternary salts with loss of methyl alcohol leads, as shown below, not to methylstrychnidinium salts, but to an isomeric series.

A curious property of methoxymethyldihydrostrychnidine is the fact that, while the direct action of methyl iodide yields the methiodide just mentioned, an entirely different result is obtained when methyl iodide acts on the methyl-alcoholic solution of the base. In these circumstances, two *oxymethoxymethyldihydrostrychnidines*, $C_{23}H_{30}O_3N_2$, namely (A), m. p. 235°, and (B), m. p. 270°, are produced; the former is convertible into the latter in a variety of ways, for example, by merely boiling with xylene. The investigation into the constitutions of these substances and the significance of these curious changes has not yet been completed.

Although methoxymethyldihydrostrychnidine combines with methyl sulphate with difficulty and is only gradually converted into the monomethosulphate under ordinary conditions, it is remarkable that it yields a substance, $C_{23}H_{30}O_2N_2,2Me_2SO_4$, evidently a mixture of two *dimethosulphates* (A) and (B), when its solution in dry benzene is boiled with methyl sulphate for several hours; of these, only the one (A) and its derivatives have so far been obtained in a pure condition. When sodium iodide is added to the aqueous solution of

the mixed dimethosulphates, the *dimethiodide* (A), $C_{23}H_{30}O_2N_2,2MeI$, m. p. 297° (decomp.), is precipitated and readily obtained pure. The *dimethochloride* (A), $C_{23}H_{30}O_2N_2,2MeCl,3H_2O$, obtained from the dimethiodide by the action of silver chloride, crystallises from water in glistening prisms and is decomposed by boiling with methyl-alcoholic potash with loss of two molecules of methyl chloride and regeneration of methoxymethyldihydrostrychnidine. It is evident that the dimethochloride must have the formula

$$C_{20}H_{22}O(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ NMe \end{matrix} \right\rangle Cl_2,$$

and since, on decomposition as just described, each nitrogen atom loses a methyl group in the form of methyl alcohol and no rings are broken, it is apparent that the heterocyclic ring system of methoxymethyldihydrostrychnidine is one possessing quite unusual stability. When, however, the dry dimethochloride (A) is heated, it loses two molecules of methyl chloride and methyl alcohol and yields *methyl-ψ-strychnidine* (see below). Methoxymethyldihydrostrychnidine, dissolved in dilute methyl-alcoholic potash, is readily oxidised by hydrogen peroxide with the formation of *methoxymethylstrychnidonic acid*, $C_{21}H_{28}O_5N_2$, a gum which is evidently an amino-acid, because, on slow evaporation of its aqueous solution, it is converted into *anhydromethoxymethylstrychnidonic acid*, $C_{21}H_{26}O_4N_2$, which crystallises well from alcohol and melts at 222°.

The further investigation of this interesting substance is in progress.

Ethoxymethyldihydrostrychnidine.—In order to determine whether a process similar to the formation of methoxymethyldihydrostrychnidine would occur if ethyl alcohol were substituted for the methyl alcohol used in the preparation of this substance, strychnidine methosulphate was digested with ethyl-alcoholic potash; a substance was then obtained which melted at about 98° and proved to be ethoxymethyldihydrostrychnidine, $C_{24}H_{32}O_2N_2$. This substance differs from the corresponding methoxy-derivative in the absence of the facility for crystallisation so remarkable in the latter and also in its greater instability on exposure to the air, whereby it rapidly becomes dark purple; it was therefore not further investigated.

Methyl-ψ-strychnidine, $C_{22}H_{26}ON_2$.—This interesting base is obtained when methoxymethyldihydrostrychnidine dimethochloride (see above) is heated and also by heating methyl*neo*strychnidinium chloride (A) or (B) (see p. 1593). It melts at 203—204° and forms well-defined salts, of which the *hydriodide*, $C_{22}H_{26}ON_2,HI$, is characteristic.

The *methiodide*, $C_{22}H_{26}ON_2,MeI$, produced by the direct com-

bination of the base with methyl iodide, also crystallises well, and is converted by silver chloride into the corresponding *methochloride*, which decomposes on heating into methyl chloride and the base. Methyl-ψ-strychnidine is not changed by electrolytic reduction, but is readily and almost quantitatively oxidised by permanganate to *strychnidone*, $C_{21}H_{24}O_3N_2$, an atom of carbon being lost during the process. This substance crystallises well, melts at 152°, and yields a *monoxime*, $C_{21}H_{25}O_3N_3$, and a *disemicarbazone*, $C_{23}H_{30}O_3N_8$; it is characterised by being remarkably resistant to further oxidation by permanganate. When it is boiled with methyl-alcoholic potash, it is converted into an isomeride, allo-*strychnidone*, m. p. 260—265°, which is no longer capable of combining either with hydroxylamine or with semicarbazide.

*The Methyl*neo*strychnidinium Salts* (A) *and* (B).—When methoxymethyldihydrostrychnidine is boiled with dilute sulphuric acid, methyl alcohol is eliminated and a solution is obtained which evidently contains the quaternary *methyl*neo*strychnidinium sulphates* (A) and (B), and this solution does not give any precipitate on the addition of ammonia or caustic potash. On adding excess of sodium iodide, *methyl*neo*strychnidinium iodide* (A) is precipitated, the isomeride (B) remaining in solution. The iodide (A) crystallises well from water, melts at about 300° (decomp.), and is converted by silver chloride into *methyl*neo*strychnidinium chloride* (A), $C_{22}H_{27}ON_2Cl,3H_2O$, which separates from water in splendid, glistening, prismatic needles, for the description and measurement of which (p. 1612) we are indebted to Dr. T. V. Barker. When this chloride is digested with methyl-alcoholic potash, it adds on methyl alcohol with the formation of methoxymethyldihydrostrychnidine (m. p. 126°), but if the dry chloride is heated it loses hydrogen chloride, and methyl-ψ-strychnidine (m. p. 203°) remains in an almost pure condition. *Methyl*neo*strychnidinium iodide* (B), $C_{22}H_{27}ON_2I$, is obtained when the mother-liquor from the separation of the isomeride (A, see above) containing sodium iodide is mixed with much 50% aqueous potassium hydroxide. This substance separates from acetone as a sandy, crystalline precipitate, m. p. 277° (decomp.), and is converted by silver chloride into *methyl*neo*strychnidinium chloride* (B), $C_{22}H_{27}ON_2Cl,H_2O$, m. p. 255° (decomp.), which, unlike the isomeride (A), exhibits little facility for crystallising. When it is digested with methyl-alcoholic potash, it is converted into methoxymethyldihydrostrychnidine and, on heating in a test-tube, it yields methyl-ψ-strychnidine. This reaction shows that the latter base may be represented by the formula $C_{20}H_{21}O(:NMe)<\begin{matrix}CH_2\\N\end{matrix}$, but the elimination of methyl alcohol may not be a simple process

involving the formation of a double bond. The difficulty is that methyl-ψ-strychnidine is unchanged by electrolytic reduction, whereas methoxymethyldihydrostrychnidine yields a dihydro-derivative under similar conditions.

Methoxymethyltetrahydrostrychnidine, $C_{23}H_{32}O_2N_2$.—This substance is obtained when methoxymethyldihydrostrychnidine is reduced electrolytically; it melts at 220° and is characterised by the facility with which it crystallises, separating, for example, from xylene in brilliant prisms. Considered as a strong base, it is mono-acid and yields a *hydriodide*, $C_{23}H_{32}O_2N_2$,HI, and a *methiodide* (*a*), $C_{23}H_{32}O_2N_2$,MeI, m. p. 227°, both of which crystallise well. The *methochloride* (*a*), prepared from the methiodide (*a*) with silver chloride, is a readily soluble, waxy, crystalline substance which is decomposed by boiling methyl-alcoholic potash with elimination of methyl chloride and separation of methoxymethyltetrahydrostrychnidine. When this base is boiled with dry benzene and excess of methyl sulphate for 20 hours, it yields a horny mass, which is a mixture of the two dimethosulphates (A) and (B), and the benzene solution gradually deposits crystals of the dimethosulphate (A). The horny mass, dissolved in water, yields on the addition of sodium iodide the *dimethiodide* (A), m. p. 315° (efferv.), the isomeride (B) remaining in solution. From the dimethiodide (A) the *dimethochloride* (A) was prepared with the aid of silver chloride as an indefinite crystalline mass which, when heated, loses two molecules of methyl chloride and methyl alcohol and yields *methyl-ψ-dihydrostrychnidine*, $C_{22}H_{28}ON_2$, m. p. 212° (compare p. 1596).

Methoxymethyltetrahydrostrychnidine dimethiodide (B) is precipitated from the mother-liquors of (A), containing sodium iodide, by the addition of a large excess of caustic potash (50%) and separates from alcohol in prisms. This dimethiodide (B) melts at 165°, and at about 230° loses both molecules of methyl iodide with regeneration of methoxymethyltetrahydrostrychnidine. If, however, the dimethiodide (B) is boiled with mesitylene, only one molecule of methyl iodide escapes, and a *methiodide* (*b*) of methoxymethyltetrahydrostrychnidine separates which has m. p. 325° (decomp.) and is isomeric with the methiodide (*a*) produced by the direct combination of the base with methyl iodide (see above). The methiodide (*b*), on heating at 250°, loses methyl iodide with formation of methoxymethyltetrahydrostrychnidine. The *dimethochloride* (B) obtained from the dimethiodide (B, m. p. 165°) by the action of silver chloride is a horny mass which, when heated in a test-tube, behaves differently from the dimethochloride (A) (see above), since it decomposes simply into methyl chloride and methoxymethyltetrahydrostrychni-

The most probable explanation of the isomerism of the dimethosalts of the series (A) and (B) is that they are stereoisomerides corresponding to the formula $C_{20}H_{24}O(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ NMe \end{matrix} \right\rangle I_2$, since it is clear that the formation of the di-quaternary salts involves the appearance of a new asymmetric nitrogen atom. The reactions of the methiodides (*a*) and (*b*) show, however, that they are structurally different, and it will be convenient at this stage to mention briefly the methods and arguments which we employ in this and similar cases; some aspects of the matter are also discussed in the following communication (see p. 1633). The presence of an aromatic nucleus bearing the –N·CO– group is the cause of important reactions, many of which were first observed by Tafel. The dichromate reaction (bluish-violet to reddish-violet) in moderately concentrated sulphuric acid solution is characteristic of strychnine; it is not given by strychnidine or its derivatives. On the other hand, these give a crimson coloration when a little potassium dichromate is added to their solutions in dilute sulphuric acid. Closely allied to this is the crimson colour developed in dilute hydrochloric acid solutions of strychnidine derivatives on the addition of ferric chloride. With strychnine, this reaction is completely negative. Finally, strychnidine derivatives, but not strychnine, couple with diazonium salts to give characteristic azo-compounds. In this connexion, we have usually employed diazobenzenesulphonic acid as the reagent, and the alkaline or neutral solutions are then yellow or orange, becoming bluish-red on the addition of a mineral acid. Incidentally it may be mentioned that Tafel's view of the nature of methylstrychnine receives support from the circumstance that this substance couples readily with diazobenzenesulphonic acid. The behaviour of strychnidine derivatives in these reactions is very much influenced by the concentration of acid in the solution, and this again harmonises with the view that we are observing the reactions of a tertiary aromatic amine. Thus in strong hydrochloric acid solution strychnidine does not form azo-compounds and is not affected by ferric chloride. In the latter case, the red colour appears on dilution of the solution, and many strychnidine and brucidine derivatives show a similar behaviour. Tetrahydrostrychnine fails to exhibit these colour reactions at a smaller acid concentration than is necessary to inhibit the strychnidine reactions, whilst, in connexion with other work not described in this communication, strychnidine derivatives have been obtained which only exhibit the ferric chloride reaction in very dilute hydrochloric acid solution and will not couple with diazo-salts in acid solution unless an excess of sodium acetate is introduced. Analogies with the already ascertained

behaviour of aromatic amines suggest that when, for example, strychnidine is dissolved in hydrochloric acid of such a strength that the ferric chloride reaction fails, the explanation is that the base is present in the solution as the dihydrochloride. We already know (see above) that the nitrogen atom not joined to the aromatic nucleus is the more basic of the two which are present in the molecule. Important confirmation of this view is derived from the fact that without exception the dimetho-salts of strychnidine derivatives do not couple with diazonium salts and do not give the ferric chloride reaction. Reverting to the question of the constitutions of the methiodides (*a*) and (*b*) of methoxymethyltetrahydrostrychnidine, it is clear that we might expect one of these, that which contains a quaternary ammonium group attached to the benzene ring, to give negative results in the colour tests. Actually, after conversion into methochloride, the methiodide (A) couples easily with diazobenzenesulphonic acid and exhibits a good ferric chloride reaction. The behaviour of the salt is closely similar to that of the parent base. On the other hand, the methochloride from the methiodide (*b*) did not give entirely negative results in the tests, but the colours were developed much more slowly and did not reach the intensity observed in the case of the (*a*) salt. We conclude that the methiodide (*a*) is $C_{20}H_{24}O(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ | \\ N \end{matrix} \right\rangle I$, whilst the methiodide (*b*), which may not be entirely homogeneous, is

$$C_{20}H_{24}O(OMe)(:NMe)\left\langle \begin{matrix} CH_2 \\ | \\ NMe \end{matrix} \right\rangle I.$$

It is shown in the following communication that the corresponding brucidine derivatives behave differently.

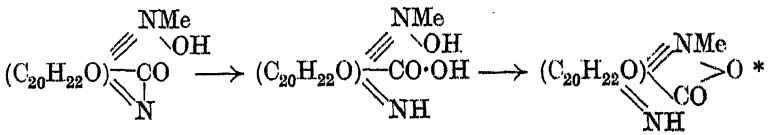
Methyl-ψ-dihydrostrychnidine, obtained either from methoxymethyltetrahydrostrychnidine dimethochloride (A) or from methyl-*neo*dihydrostrychnidinium chloride (see below) by heating, melts at 212° and yields a *methiodide*, $C_{22}H_{28}ON_2,MeI$, m. p. 335° (decomp.); the corresponding *methochloride* decomposed on heating, yielding a black syrup from which nothing definite could be isolated. Methyl-ψ-dihydrostrychnidine is clearly $C_{20}H_{23}O(:NMe)\left\langle \begin{matrix} CH_2 \\ | \\ N \end{matrix} \right\rangle$, but it is not yet certain that it is the dihydro-derivative of methyl-ψ-strychnidine. Further evidence on this point is at present being sought.

*The Methyl*neo*dihydrostrychnidinium Salts.*—As explained in the experimental section, these salts could not be directly obtained from methoxymethyltetrahydrostrychnidine, because this substance, in contrast to the methoxydihydro-base, is not decomposed by boiling with dilute sulphuric acid. The hydriodide of the methoxytetrahydro-base decomposes, however, on heating, yielding methyl

alcohol and *methyl*neo*dihydrostrychnidinium iodide*, m. p. 350° (efferv.), the hot aqueous solution of which gives no precipitate with aqueous potassium hydroxide.

On treatment with silver chloride, this yields *methyl*neo*dihydrostrychnidinium chloride*, which, on heating, is decomposed into hydrogen chloride and methyl-ψ-dihydrostrychnidine (m. p. 212°).

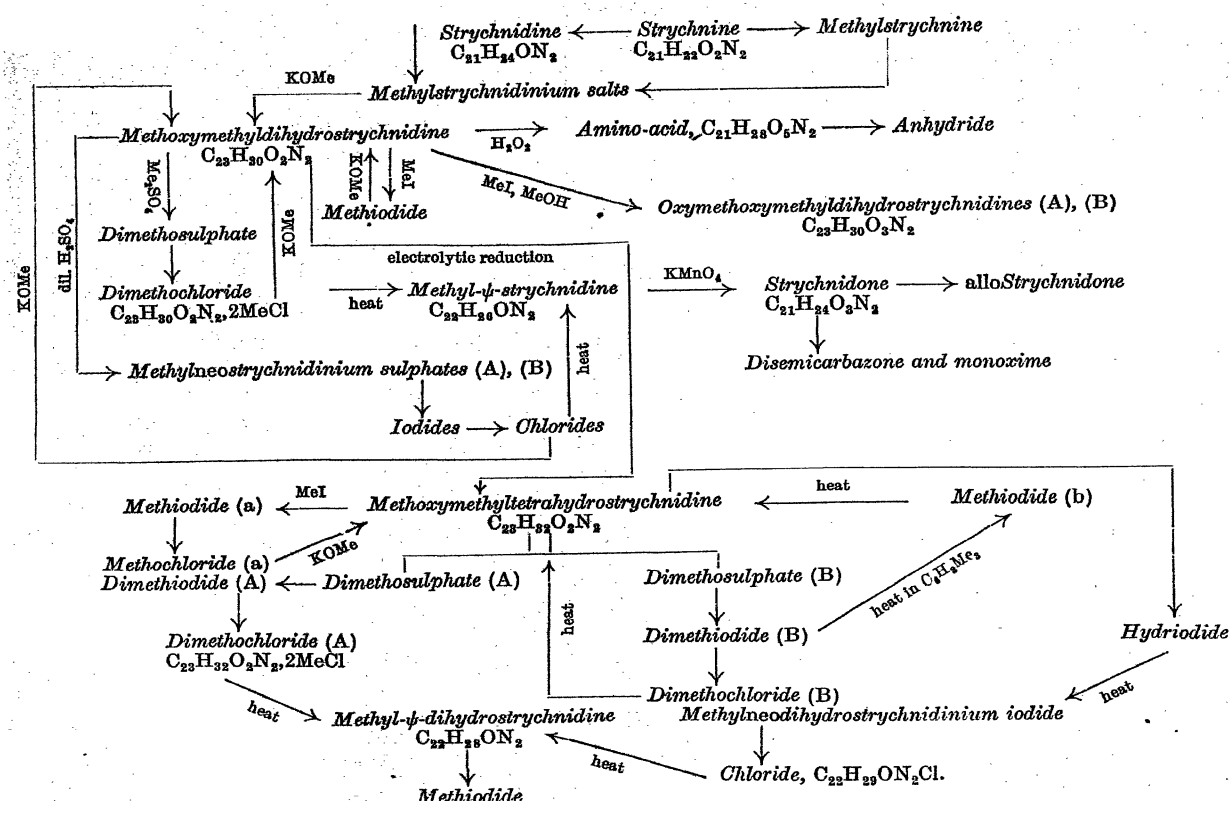
Methylstrychnine, $C_{22}H_{26}O_3N_2,4H_2O$.—This substance was first prepared by Tafel (*Ber.*, 1890, **23**, 2732), who obtained it from strychnine methiodide by decomposition with silver sulphate, followed by removal of the sulphuric acid by baryta and concentration of the filtrate; as the result of an extended examination (*Annalen*, 1891, **264**, 62), Tafel concluded that the formation of this substance from strychnine was best represented by the scheme :



Methylstrychninium hydroxide. *Methylstrychnine.*

We have found that methylstrychnine may be obtained directly by simply mixing a solution of strychnine methosulphate with caustic potash, and it has therefore become an easily accessible substance. During an examination of methylstrychnine we observed that it decomposed, on heating under reduced pressure, with elimination of methyl alcohol and formation of a substance, $C_{21}H_{22}O_2N_2$, isomeric with strychnine, for which we suggest the name *normethylstrychnine*. This base has not yet been obtained in a crystalline condition, but it yields a *methiodide*, $C_{21}H_{22}O_2N_2$,MeI, m. p. 315° (decomp.), and a *methochloride*, both of which are crystalline. When methylstrychnine, mixed with methyl-alcoholic potassium hydroxide, is heated gradually to 250°, a considerable quantity of indole is formed, and after this has been removed by steam distillation, the residue, on heating with soda-lime, yields a further amount of indole and also a small quantity of carbazole. Methylstrychnine is decomposed by heating with soda-lime, with the formation of a base, $C_{10}H_{11}N$, b. p. 93°/25 mm., which yields a picrate, m. p. 168°, and appears to be an ethylindole; carbazole is also produced in small quantity during this decomposition. The electrolytic reduction of a solution of methylstrychnine in dilute sulphuric acid is described on p. 1626. After removal of the sulphuric acid by barium carbonate, the crystalline *methylstrychnidinium*

* In accordance with our present-day conceptions regarding the nature of betaines, methylstrychnine is a dipole and it is no longer necessary to assume propinquity of the groups $\cdot CO_2$ and $\cdot NMe$.


Strychnidine C21H24ON2
Strychnine C21H22O2N2
Methylstrychnine
KOMe
Methylstrychnidinium salts
Methoxymethyldihydrostrychnidine C23H30O3N2
H2O2
Amino-acid, C21H28O5N2
Anhydride
Me2SO4
KOMe
MeI
Methiodide
MeI, MeOH
Oxymethoxymethyldihydrostrychnidines (A), (B) C23H30O3N2
dil. H2SO4
Dimethosulphate
KOMe
electrolytic reduction
KMnO4
Strychnidone C21H24O3N2
alloStrychnidone
Dimethochloride C25H30O2N2,2MeCl
heat
Methyl-ψ-strychnidine C22H26ON2
Disemicarbazone and monoxime
Methylneostrychnidinium sulphates (A), (B)
heat
Iodides
Chlorides
MeI
heat
Methiodide (a)
Methoxymethyltetrahydrostrychnidine C23H32O2N2
Methiodide (b)
KOMe
Methochloride (a)
Dimethiodide (A)
Dimethosulphate (A)
Dimethosulphate (B)
heat in C6H4Me2
heat
Dimethochloride (A) C23H32O2N2,2MeCl
Dimethiodide (B)
Hydriodide
Dimethochloride (B)
heat
heat
Methyl-ψ-dihydrostrychnidine C22H28ON2
Methylneodihydrostrychnidinium iodide
heat
Chloride, C22H29ON2Cl.
Methiodide

hydrogen carbonate, $C_{22}H_{27}ON_2,HCO_3,H_2O$, is obtained, and this is decomposed by boiling methyl-alcoholic potash, yielding methoxymethyldihydrostrychnidine (m. p. 126°). On treatment with acids the carbonate yields the same strychnidine metho-salts as are obtained from strychnidine methosulphate by decomposition with sodium iodide and other salts.

Whilst it is clearly possible to develop arguments bearing on the structure of strychnine and brucine from the new facts brought to light in this and the following investigation, we prefer to postpone such theoretical deductions until further experimental data are available. The annexed table illustrates the more important relationships described in this memoir.

Experimental.

Strychnine Methosulphate, $C_{21}H_{22}O_2N_2,Me_2SO_4$.—Finely powdered strychnine (50 g.) is mixed with methyl alcohol (250 c.c.), and freshly distilled methyl sulphate (50 g.) added with shaking; the base then dissolves completely and the temperature rises about 17°. The *methosulphate*, which soon begins to separate, is collected after 24 hours, washed twice with a little methyl alcohol, and dried on the steam-bath (yield, 60 g.). The substance discolours at 270—280° and decomposes with effervescence at about 282°. It is very soluble in hot water and separates, on cooling, in quadrilateral plates; it also dissolves readily in hot methyl alcohol and crystallises therefrom in groups of glistening needles. The solution in sulphuric acid (60% by vol.) gives with dichromate an intense purple colour, changing to brown (Found: C, 59·7; H, 6·0; N, 6·3. $C_{21}H_{22}O_2N_2,Me_2SO_4$ requires C, 60·0; H, 6·1; N, 6·1%).

Strychnine Methobromide.—When concentrated aqueous solutions of the methosulphate and sodium bromide are mixed, the *methobromide* separates immediately. It is readily soluble in hot water, from which it crystallises as a voluminous mass of glistening needles; it discolours at 300° and melts at about 320° (efferv.) (Found in material dried at 110°: C, 61·3; H, 5·9. $C_{21}H_{22}O_2N_2,MeBr$ requires C, 61·5; H, 5·8%).

The aqueous solution of the methosulphate gives with sodium iodide an immediate precipitate of strychnine methiodide, which separates from much water in glistening, pearly cubes, darkens at 300°, and effervesces at about 320° (compare Stahlschmidt, *Pogg. Ann.*, 1859, **108**, 513; Tafel, *Ber.*, 1890, **23**, 2733).

Strychnidine and Tetrahydrostrychnine.—The following process for the preparation and separation of these substances is a considerable improvement on that recommended by Tafel (*Annalen*, 1898, **301**, 303, 316).

Strychnine (150 g.), dissolved in sulphuric acid (900 g.) and water (600 c.c.), was placed in the cathode chamber of the electrolytic reduction apparatus described in Part II of this research (J., 1924, **125**, 1798) and reduced for 16 hours at 18° by a current of 5 amps. The product was diluted with ice, filtered, made alkaline with a large excess of concentrated caustic soda solution, and the resulting granular precipitate was collected, washed well with water, and dried on the steam-bath. The mixture was then extracted with boiling alcohol (1 litre) and quickly filtered; on cooling, a crystalline precipitate separated (34 g.); from the concentrated mother-liquor, a further 20 g. was obtained.

This colourless crystalline mass, which, after drying at 100° had m. p. 183—185°, was recrystallised from benzene (700 c.c.); the nearly colourless crystals which separated (36 g.) melted at 202° and proved to be pure tetrahydrostrychnine (Found: C, 74·5; H, 7·7. $C_{21}H_{26}O_2N_2$ requires C, 74·5; H, 7·7%). The benzene mother-liquor was evaporated to dryness, and the residue, on crystallisation from alcohol, yielded a voluminous mass of white needles (17 g.), m. p. 244—245°. The residue from the first alcoholic extract, crystallised from alcohol, in which it was sparingly soluble, gave, after the mother-liquors had been worked up, a further quantity (53 g.) of the same substance, m. p. 243—245°. The two portions were mixed and crystallised from alcohol, pure strychnidine, m. p. 246°, being readily obtained.

Strychnidine Hydriodide.—When strychnidine is shaken with dilute sulphuric acid, a crystalline mass of the sulphate results, and, if this is dissolved in hot water and sodium iodide added, a voluminous mass of needles separates. This is collected, washed, dried, and recrystallised from boiling alcohol, in which the *hydriodide* is sparingly soluble, crystallising in stars of glistening needles (Found: C, 56·6; H, 5·6. $C_{21}H_{24}ON_2,HI$ requires C, 56·3; H, 5·6%). This hydriodide is sparingly soluble in boiling water and the solution gives an immediate precipitate with ammonia. It discolours at 275—280°, is nearly black at 290°, and decomposes at about 305° to a black froth.

Strychnidine Methosulphate.—This substance has been prepared in two ways: (i) by direct union and (ii) by the electrolytic reduction of strychnine methosulphate.

(i). Strychnidine (40 g.) is mixed with methyl alcohol (250 c.c.), freshly distilled methyl sulphate (40 g.) added, and the whole shaken and warmed at 40—50°; all passes into solution and suddenly the *methosulphate* commences to separate. After 12 hours, the precipitate is collected, washed with a little methyl alcohol, and recrystallised from this solvent (Found in material dried at

100°: C, 61·2; H, 6·6. $C_{21}H_{24}ON_2,Me_2SO_4$ requires C, 61·8; H, 6·7%).

(ii). Strychnine methosulphate (10 g.), dissolved in sulphuric acid (100 c.c. of 30% by vol.), is reduced in the usual electrolytic cell (p. 1600) by a current of 5 amps. for 16 hours. The clear, almost colourless solution is diluted with water, boiled with excess of barium carbonate, and filtered, and the filtrate and washings are concentrated to a small bulk; the mass of crystals that gradually separates is crystallised from methyl alcohol (Found in material dried at 100°: C, 61·6; H, 6·9; N, 6·4%).

The identity of the methosulphates produced in (i) and (ii) was shown (1) by conversion into identical methobromides and methiodides, and (2) by both yielding methoxymethyldihydrostrychnidine (m. p. 126°) by the action of methyl-alcoholic potash (p. 1602).

The *methobromide* is prepared by mixing a warm, saturated solution of strychnidine methosulphate with sodium bromide; the clear solution slowly deposits a woolly mass of needles, which is washed with water containing a trace of sulphurous acid and dried at 100°. The substance does not melt at 300° (Found: C, 63·9; H, 6·5. $C_{21}H_{24}ON_2,MeBr$ requires C, 63·6; H, 6·5%).

The methiodide separates as a voluminous mass of needles when sodium iodide is added to a hot aqueous solution of the methosulphate; on boiling, a clear solution is obtained from which the methiodide separates as a woolly mass of needles. This substance has already been described by Tafel (*Annalen*, 1898, **301**, 314), who obtained it by direct union of strychnidine with methyl iodide. It decomposes at about 325° to a brown froth.

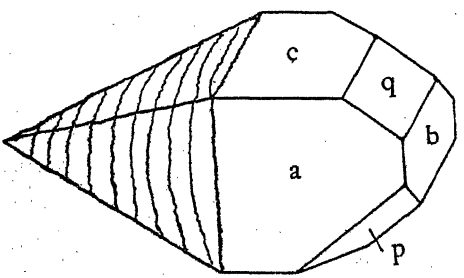
The Methochloride.—The methiodide just described is readily soluble in boiling water, and on addition of silver chloride and digestion on the steam-bath for an hour decomposition is complete. The filtrate from the silver salts, on evaporation to a small bulk, deposits the very readily soluble *methochloride* in needles. These are collected and dissolved in a very little hot water and the solution is rapidly cooled; it sets to a jelly which gradually changes to colourless needles. The substance, dried at 100°, is a horny mass which begins to darken at 260°, is dark brown at 300°, and decomposes with effervescence at 310° (Found: C, 70·8; H, 7·3. $C_{21}H_{24}ON_2,MeCl$ requires C, 71·1; H, 7·3%). When the dry, powdered methochloride was carefully heated in a test-tube over a free flame, a gas, which burnt with a green-edged flame, was given off and a considerable crystalline sublimate formed. The residual brown syrup crystallised in contact with methyl alcohol, separated from this solvent in needles, melted at 248—250°, and proved to be strychni-

dine (Found: C, 78·2; H, 7·6%), but, owing to considerable decomposition, the yield was a small one.

Methoxymethyldihydrostrychnidine.

Strychnidine methosulphate (20 g.) is mixed with methyl-alcoholic potash (120 c.c. of 25%) and heated in an open flask in a rapidly boiling water-bath; the clear solution gradually clouds and, after 30 minutes, the well-cooled viscid product gives, on dilution with ice and water (600 c.c.), a caseous precipitate, which is washed well and allowed to dry on porous porcelain at the ordinary temperature. The nearly colourless mass, which melts at about 115—119° and is pure enough for many purposes, is rather readily soluble in boiling methyl alcohol, and separates, on slowly cooling, in highly characteristic, large, glistening, pale purple prisms. For reasons explained on p. 1603, it is advisable to dissolve the substance as rapidly as possible in the methyl alcohol and cool the filtered solution quickly by shaking it in a corked flask in contact with ice and water; after being washed with a little methyl alcohol, the crystalline meal is then only slightly coloured (Found: C, 75·4; H, 8·2; N, 7·5; MeO, 8·2. $C_{23}H_{30}O_2N_2$ requires C, 75·4; H, 8·2; N, 7·6; MeO, 8·4%). *Methoxymethyldihydrostrychnidine* melts at 125—126° and the crystals become pale purple when exposed to the air or more rapidly when heated on a watch-glass on the steam-bath. It is readily soluble in boiling alcohol or benzene, sparingly soluble in cold acetone, ether, or ligroin, and separates well in hard crusts of striated, pale lilac-brown prisms when ligroin is added to a boiling solution in benzene.

FIG. 1.



Crystals which had separated slowly from methyl alcohol were kindly examined by Dr. T. V. Barker, who found them to be monoclinic with the highly characteristic habit shown in Fig. 1. The right-hand termination consists of plane faces, whilst the other gradually tapers to a point in a series of curved surfaces. The crystals are all of one kind, the mirror-image form being no doubt proper to the hitherto unsynthesised enantiomeride. The forms developed are $a(100)$, $b(010)$, $c(001)$, $q(011)$ and, not infrequently, $p(111)$. The elements $a : b : c = 0{\cdot}7646 : 1 : 0{\cdot}6864$, $\beta = 109° 6'$

were computed from the following mean results of measurement of four crystals :

	b(010)	a(100)	c(001)	q(011)	p(1̄11)
ϕ	Polar.	0° 0′	*70° 54′	70° 54′	*121° 7′
ρ	Face.	90 0	90 0	*57 2	59 29 (+5)

Optically the axial plane is b(010) with medium axial angle and positive double refraction.

The salts of methoxymethyldihydrostrychnidine are very readily soluble and a solution of a trace of the base in dilute sulphuric acid gives with a drop of dichromate or concentrated nitric acid an intense crimson coloration, the same coloration being also produced when a solution in dilute hydrochloric acid is warmed with ferric chloride. The solution in glacial acetic acid is not precipitated by water and the base separates on the addition of ammonia as a voluminous mass resembling alumina. *The hydriodide.* When the base, dissolved in a slight excess of dilute sulphuric acid, is mixed with sodium iodide, a yellow to brown coloration rapidly develops, due evidently to oxidation. A nearly pure specimen of the hydriodide was obtained by adding a little sulphurous acid to a solution of the base in dilute sulphuric acid and then precipitating the salt with sodium iodide. The precipitate was rapidly collected and recrystallised from water containing sulphurous acid, separating as a colourless, granular powder. This was collected as rapidly as possible, washed with very dilute sulphurous acid, transferred to porous porcelain, and left over sulphuric acid in a desiccator evacuated to 1 mm. Even then, the substance became slightly yellow, but the salt could now be dried at 100° without further discoloration (Found : C, 56·1; H, 6·2. $C_{23}H_{30}O_2N_2,HI$ requires C, 55·9; H, 6·3%). This hydriodide melts at 203° (decomp.).

In the course of a large number of preparations of methoxymethyldihydrostrychnidine, it was always observed that only about 70% of the weight of the crude substance separated during the first crystallisation from methyl alcohol, and still less separated if the boiling with the solvent was prolonged. When the dark purple mother-liquors from several preparations were evaporated to dryness and the residual gum was distilled under reduced pressure, a considerable amount (35 g.) passed over at about 240—260°/2 mm.; from a solution of this in hot methyl alcohol, crystals (5 g.) of methoxymethyldihydrostrychnidine (m. p. 126°) separated. The mother-liquor was again distilled and the fraction 240—250°/1 mm. dissolved in boiling methyl alcohol; on rubbing and keeping for some days, nearly colourless prisms separated (6 g.) which melted at 202—203° after crystallisation and proved to be *methyl-ψ-strychnidine* (Found :

C, 78·8; H, 7·7; N, 8·5. $C_{22}H_{26}ON_2$ requires C, 79·0; H, 7·8; N, 8·4%) (compare p. 1609). On redistilling the mother-liquor of this substance, successive quantities of methoxymethyldihydrostrychnidine (2 g.) and methyl-ψ-strychnidine (2·3 g.) were obtained and also a small quantity of a substance, m. p. 295° (decomp.), which is evidently *oxymethoxymethyldihydrostrychnidine* (Found: C, 72·0; H, 8·0; N, 7·3. $C_{23}H_{30}O_3N_2$ requires C, 72·3; H, 7·8; N, 7·3%) (compare p. 1608). In connexion with the above observations, it was found that methoxymethyldihydrostrychnidine may be distilled without loss of methyl alcohol or other decomposition, and passes over at 235—237°/1 mm. as a colourless syrup, which may set to a resin or become a mass of crystals. The crystals melt, without recrystallisation, at 124—126°, contain C, 75·4; H, 8·2, and show no depression in m. p. after admixture with a specimen crystallised from methyl alcohol.

The distillation of the crude product of the action of methyl-alcoholic potash on strychnidine methosulphate was then investigated, and it was found that this passes over almost without residue at about 240—250°/1 mm. and crystallises at once. This procedure obviates the loss attendant on the crystallisation from methyl alcohol, since the distilled substance is pure enough for most purposes.

Methoxymethyldihydrostrychnidine Methiodide, $C_{23}H_{30}O_2N_2$,MeI.—For reasons explained on p. 1607, this substance must be prepared in the absence of methyl alcohol. The base (10 g.) is heated under reflux with carefully purified methyl iodide (10 c.c.) and the clear solution in about an hour begins to deposit crystals. The mass (12 g.) is collected, washed with methyl iodide, and dried on the steam-bath; m. p. about 275—278° (decomp.) (Found: C, 56·5; H, 6·5; I, 25·4. $C_{23}H_{30}O_2N_2$,MeI requires C, 56·7; H, 6·5; I, 25·0%). This substance does not appear to undergo change when it is crystallised from methyl alcohol, since the large brown prisms which separate melt at 278° (decomp.). It is sparingly soluble in cold, but readily soluble in hot, water and separates on slow cooling in pink, well-developed, arrow-shaped prisms.

In view of the fact that methoxymethyldihydrobrucidine combines with 2 mols. of methyl iodide at 140° (p. 1629), methoxymethyldihydrostrychnidine (5 g.), dissolved in carefully purified methyl iodide (15 c.c.), was heated in a sealed tube at 130° for 7 hours; the purple solution, on cooling, gradually deposited a crust of purple crystals which, after being washed with methyl iodide, had m. p. 265—270° (decomp.) and consisted of the monomethiodide (Found: C, 57·0; H, 6·4%). When this substance was crystallised from water and the mother-liquor allowed to stand exposed to the air, a crust of nodules gradually separated, which melted at 175°

(decomp.), became solid again, and then melted at about 240—250° (decomp.).

This substance appears to be the methiodide crystallising with 1 mol. H_2O which is not lost at 100° (Found: C, 55·0; H, 6·3. $C_{23}H_{30}O_2N_2$,MeI,H_2O requires C, 54·7; H, 6·6%). The methyl iodide mother-liquors from the substance m. p. 265—270° (decomp.) gave, on concentration, a little more of the same substance and then a crystalline crust, m. p. 235°, containing a mere trace of iodine (Found: C, 71·6; H, 7·7%), and this substance is evidently identical with the oxymethoxymethyldihydrostrychnidine described on p. 1608.

Methoxymethyldihydrostrychnidine Methohydroxide, $C_{23}H_{30}O_2N_2$,MeOH.—When the methiodide just described is heated on the steam-bath with water and excess of silver chloride, and the filtrate from the silver salts is evaporated, a syrup remains (which was not analysed) which doubtless contains the methochloride. Boiling methyl-alcoholic potash (25%) decomposes this and, on the addition of water, a resin separates. This is dissolved in boiling methyl alcohol, and the solution, after being concentrated and left in the ice-chest, deposits balls of colourless needles, m. p. 113°; on recrystallisation, the substance melts at 116—117° (Found: C, 72·4; H, 8·7; N, 6·8. $C_{24}H_{34}O_3N_2$ requires C, 72·4; H, 8·8; N, 7·0%). The same substance is formed, but less readily, when the methiodide is digested with methyl-alcoholic potash. The *methohydroxide* is very readily soluble in benzene, rather less readily in boiling petroleum, and sparingly even in boiling water. The solution in sulphuric acid (60% by vol.) gives with dichromate an immediate intense crimson colour; in dilute hydrochloric acid, ferric chloride produces an eosin coloration, becoming intense crimson on warming. The solution in dilute nitric acid (30%) is pink, becoming deeper on standing or warming and intense crimson and then green on boiling, and, on addition of ammonia, a yellow, crystalline base separates. When the methohydroxide is heated, it effervesces between 200° and 215°, yielding a brown syrup which sets to a resin on cooling and has not been examined. The methohydroxide dissolves readily in dilute hydrochloric acid and the solution gives, with sodium iodide, a gum, which soon crystallises and separates from methyl alcohol in glistening prisms of the methiodide, m. p. 278° (decomp.) (Found: C, 56·8; H, 6·6. Calc.: C, 56·7; H, 6·5%).

Methoxymethyldihydrostrychnidine Dimethosulphate, $C_{23}H_{30}O_2N_2$,$2Me_2SO_4$, *the Dimethiodide and the Dimethochloride.*—The methoxydihydro-base does not appear to combine with methyl sulphate when it is mixed with it. Interaction is very slow even when a solution of the

base in benzene is digested with methyl sulphate; combination does, however, take place on long boiling, with formation of the dimethosulphate; in spite of careful search, it has not been found possible to isolate the mono-derivative.

The dry base (10 g.), dissolved in specially dried benzene (200 c.c.), was mixed with methyl sulphate (15 c.c.) which had been distilled immediately before the experiment, and the whole was digested in a reflux apparatus, carefully protected from moisture; the original purple solution gradually became paler and, after about 2 hours, a resinous mass began to separate. The heating was continued for 10 hours, the product allowed to remain over-night, and the benzene layer decanted from the pale lilac resin. The clear benzene solution, left in a corked flask, gradually deposited soft, circular nodules, and these were collected, rapidly washed with dry benzene, and dried over sulphuric acid in a vacuum desiccator. Analysis showed that this substance is the *dimethosulphate* (Found: C, 51·6; H, 6·7. $C_{27}H_{42}O_{10}N_2S_2$ requires C, 52·4; H, 6·8%).

The Dimethiodide (A), $C_{23}H_{30}O_2N_2$,2MeI.—A warm aqueous solution of the crude dimethosulphate gave with excess of boiling aqueous sodium iodide a clear solution, and on standing, warty masses gradually separated. After 2 days, the mass was collected, washed with a little water, drained on porous porcelain, and crystallised from methyl alcohol, from which the *dimethiodide* (A) separated in striated, glistening needles, which became opaque on the steam-bath; m. p. about 297° (decomp.) (Found: C, 46·0; H, 5·5; I, 39·4. $C_{25}H_{36}O_2N_2I_2$ requires C, 46·2; H, 5·5; I, 39·3%). This substance is very readily soluble in boiling water and appreciably soluble in the cold and separates as a sandy powder consisting of round, warty masses. The aqueous solution gives no precipitate with ammonia. The yield of the dimethiodide (A) precipitated from the solution of the dimethosulphate by sodium iodide is only 50% of that required by theory and there can be little doubt that the aqueous mother-liquor contains the dimethiodide (B) corresponding with the dimethiodide (B) of methoxymethyltetrahydrostrychnidine (p. 1620). When solid potash was added to these well-cooled mother-liquors, a caseous precipitate separated in large quantity, and on crystallising this from methyl alcohol a small amount of the dimethiodide (A) was obtained as a crust of small prisms. The bulk of the substance remained in the methyl alcohol, but all attempts to isolate the isomeride (B) in a pure state were unsuccessful. This was due partly to the presence of traces of the dimethiodide (A), but mainly to the ready solubility of the isomeride (B) and the small tendency it exhibited to crystallise in definite form.

The *dimethochloride* (A) is obtained when a hot aqueous solution of the dimethiodide (A) is heated on the steam-bath with excess of silver chloride for an hour; the filtrate from the silver salts gives, on evaporation, a solid mass which separates from a little water in large, well-developed, colourless prisms resembling sugar crystals. The air-dried substance loses 6·6% at 100°, and about the same amount when kept over phosphoric anhydride in a vacuum desiccator, the brilliant crystals becoming chalky (Calc. for $C_{25}H_{36}O_2N_2Cl_2,3H_2O$ losing $2H_2O$: H_2O, 6·9%. Found in the substance dried at 100°: C, 62·0; H, 7·6; Cl, 14·3. $C_{25}H_{36}O_2N_2Cl_2,H_2O$ requires C, 61·9; H, 7·8; Cl, 14·6%). The dry crystals give off steam at about 150° and melt at about 255—257° with evolution of gas and formation of methyl-ψ-strychnidine (p. 1609).

A solution in dilute sulphuric acid gives merely a yellow coloration with dichromate. The dimethochloride is very soluble in water or methyl alcohol, and methyl-alcoholic potash gives an immediate precipitate of potassium chloride; on boiling and addition of water, a viscid, curdy precipitate separates which gives an intense crimson colour with dilute sulphuric acid and dichromate, crystallises from methyl alcohol in prisms, m. p. 125—126°, and proves to be methoxymethyldihydrostrychnidine, the yield being nearly a quantitative one.

Oxymethoxymethyldihydrostrychnidines (A) *and* (B).—The isomeride (A, m. p. 235°) is formed in small quantity when methoxymethyldihydrostrychnidine is heated with methyl iodide (see p. 1605), but is produced much more readily and in larger quantity under the following conditions. The base (6 g.) dissolves in methyl alcohol (60 c.c.) and methyl iodide (8 c.c.) in the cold. When the solution is boiled under reflux for 3 hours and then kept for a week, glistening scales (3 g.) separate; after boiling for 3 hours and being concentrated, the mother-liquor deposits a further small quantity. The crystals are washed with methyl alcohol containing a little ammonia to remove traces of iodine, and dried on the steam-bath (Found: C, 72·3; H, 7·9; N, 6·9; MeO, 8·6. $C_{23}H_{30}O_3N_2$ containing 1MeO requires C, 72·3; H, 7·8; N, 7·3; MeO, 8·1%).

Oxymethoxymethyldihydrostrychnidine (A) melts at 235° and dissolves with some difficulty in cold dilute hydrochloric acid. It is readily soluble in glacial acetic acid and is not reprecipitated by water. A solution in dilute sulphuric acid (60% by vol.) gives an intense crimson with dichromate or a drop of concentrated nitric acid; a solution in dilute hydrochloric acid gives no immediate coloration with ferric chloride, but, on warming, a deep crimson colour develops. The substance is apparently not changed when it dissolves in dilute

hydrochloric acid, since, if ammonia is added immediately, a gelatinous precipitate separates which becomes chalky on warming and melts at 220—225°. The substance dissolves readily on boiling with alcohol, semicarbazide hydrochloride, and sodium acetate, and on addition of ammonia and warming, a crystalline precipitate separates, m. p. 275° (decomp.), containing N, 7·7%, and is evidently the isomeride (B) (see below). When the dark brown mother-liquor of the substance (A), m. p. 235°, was evaporated to a small bulk and mixed with dilute ammonia, a sticky precipitate separated which soon became crystalline. On warming this with methyl alcohol, most of it dissolved, leaving a sparingly soluble, chalky substance consisting of the isomeride (B); this separated from much methyl alcohol as a rather indefinite, crystalline powder, m. p. about 275° (decomp.) (Found: C, 72·0; H, 7·7; N, 7·1. $C_{23}H_{30}O_3N_2$ requires C, 72·3; H, 7·8; N, 7·3%).

Conversion of Oxymethoxymethyldihydrostrychnidine (A) *into* (B).—This change takes place under the following conditions: (i) When the substance (A) was boiled with a little xylene, gradual change took place and a sandy, crystalline, very sparingly soluble powder was formed, which was washed with xylene; m. p. about 280—285° (decomp.) (Found: C, 73·0; H, 7·9; MeO, 7·8%). The xylene mother-liquor, after being concentrated, slowly developed a hard crust of octahedra, m. p. 285° (decomp.); (ii) when the isomeride (A) was boiled with alcohol for about an hour, the concentrated solution gradually deposited well-defined octahedra, m. p. 280° (decomp.), and the same result was obtained on boiling with acetone, the m. p. of the crystals being about 280° (decomp.). In the last case, analysis gave C, 72·3; H, 8·3; N, 7·3; MeO, 7·8%.

Oxymethoxymethyldihydrostrychnidine (B) was also obtained when methoxymethyldihydrostrychnidine (2 g.) was boiled with nitric acid (5 c.c.), diluted with water (50 c.c.). The pale pink solution became brown, and if, after about 20 minutes, ammonia was added, a sticky precipitate separated which contained some unchanged base. On crystallising it from much alcohol and then from xylene–alcohol, colourless prisms were obtained, m. p. about 285° (decomp.) (Found: C, 72·3; H, 8·1%). The isomeride (B) was also obtained when methoxymethyldihydrostrychnidine (1·5 g.) was boiled with acetic anhydride for 10 minutes, and the solution then kept for some days. The crystalline crust which separated consisted of some unchanged base mixed with the oxy-derivative (B), and there was no sign of the formation of an acetyl derivative; on boiling the mixture with alcohol, the unchanged base dissolved and the isomeride (B) remained in an almost pure condition.

Methyl-ψ-strychnidine and the Methylneostrychnidinium Salts.

Methyl-ψ-strychnidine is obtained (i) when the mother-liquors from the crystallisation of crude methoxymethyldihydrostrychnidine are distilled (p. 1603), (ii) when methyl*neo*strychnidinium chloride is heated (p. 1612), and (iii) by the action of heat on methoxymethyldihydrostrychnidine dimethochloride (A), during which this substance loses 2 mols. of methyl chloride and methyl alcohol. The last decomposition is best carried out with small quantities of material, which must be very pure and quite free from inorganic matter; otherwise much tar is produced, the yield of product is small, and the highly coloured mass very difficult to purify. When the dimethochloride (1 g.) is cautiously heated in a wide test-tube over a free flame, a gas is given off which has a very pungent, particularly unpleasant smell and burns with a smoky, green-edged flame, and a considerable crystalline sublimate forms on the sides of the tube. This melts at about 195° and is nearly pure methyl-ψ-strychnidine.

When the effervescence has ceased, the heating is discontinued; the liquid product should then be only slightly coloured and should crystallise completely. Several such tubes are broken up and their contents extracted with much boiling alcohol (in which the product is sparingly soluble), and the solution is digested with norite for an hour and concentrated to a small bulk; the new substance gradually separates in groups of striated, pale ochre needles which become almost colourless after recrystallisation (Found: C, 79·0; H, 7·8; N, 8·6. $C_{22}H_{26}ON_2$ requires C, 79·0; H, 7·8; N, 8·4%).

Methyl-ψ-strychnidine melts at 203—204° and appears to distil under reduced pressure almost without decomposition. It is very sparingly soluble in cold acetone and not readily on boiling; the solution may be concentrated and left for a considerable time without crystallisation setting in, and then groups of needles gradually form. It dissolves very readily in benzene or petroleum and separates very gradually from these in needles. It does not appear to be affected by heating with concentrated sulphuric acid on the steam-bath for ½ hour.

The base is readily soluble in dilute acids. The solution in dilute sulphuric acid is coloured crimson by dichromate, and the same colour develops when the substance is dissolved in concentrated nitric acid. The solution in dilute hydrochloric acid gives, with ferric chloride, a pale pink colour which becomes deep crimson on warming.

The *hydriodide*, $C_{22}H_{26}ON_2,HI$, was prepared by dissolving the base in a slight excess of warm dilute sulphuric acid and then adding warm sodium iodide; on rubbing, the cloudy liquid deposited the

hydriodide as a voluminous mass of colourless crystals; these were sparingly soluble in boiling water and the solution gradually deposited crusts, which melted at 265—270° with effervescence, leaving a black mass (Found: C, 56·8; H, 5·9. $C_{22}H_{27}ON_2I$ requires C, 57·1; H, 5·9%).

This hydriodide is sparingly soluble in boiling alcohol and separates therefrom in stars of prismatic needles. The solution in hot water gives with potash an immediate precipitate of the base.

The Methiodide, $C_{22}H_{26}ON_2$,MeI.—When the base (2 g.) was mixed with methyl iodide (5 c.c.), combination took place in the cold with rise of temperature and formation of the methiodide. After warming for a few minutes and cooling in ice, the solid was collected and crystallised from methyl alcohol, from which the substance separated in almost colourless needles. These scarcely darken at 270° and melt at about 312° with effervescence to a dark brown syrup (Found: C, 57·5; H, 6·1. $C_{23}H_{29}ON_2I$ requires C, 57·9; H, 6·1%).

The *methochloride*, prepared in the usual manner by heating the methiodide with water and silver chloride, was obtained, when the solution was concentrated to a small bulk, in long, flat prisms and was very readily soluble. When it was heated in a test-tube, it gave off water and methyl chloride, and a considerable sublimate formed; the residue, on crystallising from methyl alcohol, gave methyl-ψ-strychnidine in almost colourless needles, m. p. 202—203°.

In order to determine whether methyl-ψ-strychnidine could be reduced electrolytically, the base (2·5 g.), dissolved in dilute sulphuric acid (100 c.c. of 20%), was placed in the usual electrolytic cell (p. 1600) and a current of 4 amps. passed for 6 hours. The colourless solution was mixed with excess of ammonia, and the precipitate crystallised from methyl alcohol; colourless needles (2·2 g.) were then obtained which melted at 202° and at the same temperature in admixture with methyl-ψ-strychnidine. Identity was further established by analysis (Found: C, 79·2; H, 7·6. Calc. for $C_{22}H_{26}ON_2$: C, 79·0; H, 7·8%).

The Methylneostrychnidinium Salts.—The solution of the methyl-*neo*strychnidinium sulphates (A) and (B) from which the other salts were obtained was prepared as follows: Methoxymethyldihydrostrychnidine (p. 1602; 20 g.) was dissolved in dilute sulphuric acid (300 c.c. of 10% by vol.) and heated to boiling in a flask fitted with a long, ground-in condenser. In a short time, methyl alcohol could be detected at the open end of the tube, and when, after 2 hours, all of it had boiled away, a few drops of the liquid no longer gave a precipitate or cloudiness, due to unchanged base,

on being basified. The pale brown solution was made just alkaline with ammonia, a little sulphurous acid was added, and then a boiling solution of sodium iodide (25 g.). The clear solution was rapidly filtered and vigorously stirred; *methyl*neo*strychnidinium iodide* (A) then separated either as a heavy, crystalline precipitate or sometimes as a gum which soon crystallised. On standing, a mass of crystals separated from the supernatant liquid. The solid was collected and dissolved in boiling water containing a little sulphurous acid and the solution was rapidly filtered; the iodide (A) then separated, on standing, in characteristic, long needles. After recrystallisation from water (3 g. dissolve in about 75 c.c.), the substance was dried on the steam-bath (Found: C, 56·7; H, 6·0; I, 26·9. $C_{22}H_{27}ON_2I$ requires C, 57·2; H, 5·9; I, 27·4%).

This iodide (A) darkens at 295° and decomposes at about 300° to a black mass. It is very sparingly soluble in methyl alcohol. A piece of filter-paper soaked in the aqueous solution gradually becomes yellow and then orange on exposure to air. A hot aqueous solution of the iodide gives no precipitate with caustic potash (30%); even after heating for ½ hour on the steam-bath, the iodide separates unchanged on cooling. Although so sparingly soluble in water, it dissolves readily in cold dilute hydrochloric acid and in large quantities on boiling; the solution deposits, on slowly cooling, stars of prismatic needles of a substance which decomposes at 305° and is not a hydrochloride, as was expected, but consists of the unchanged iodide (Found: C, 57·5; H, 6·0%).

*Methyl*neo*strychnidinium Chloride* (A).—The iodide (A) was ground to a paste with warm water and heated on the steam-bath with a large excess of silver chloride for 2 hours with frequent shaking. The colourless filtrate and washings from the silver salts were concentrated to a small bulk by distillation under reduced pressure, and the solution was placed over sulphuric acid in a vacuum desiccator; the chloride then gradually separated in brilliant, colourless, prismatic needles. These, after being recrystallised from very little water and dried on porous porcelain in the air, appeared to contain $3H_2O$, since the loss on heating at 100° was 12·8% (Calc. for $C_{22}H_{27}ON_2Cl,3H_2O$: loss, 12·7%). When exposed over sulphuric acid in a vacuum desiccator, the crystals became opaque and lost the whole of their water of crystallisation, since there was no further loss at 100° (Found: C, 71·5; H, 7·3. $C_{22}H_{27}ON_2Cl$ requires C, 71·3; H, 7·3%). The chloride (A) melts at about 270° with vigorous effervescence (compare p. 1609) and is very readily soluble in water; the solution, which gives no precipitate either with ammonia or with caustic potash, is intensely bitter. The solution in dilute sulphuric acid gives, with concentrated nitric acid or

dichromate, a yellow coloration which changes to crimson on warming; ferric chloride added to a solution in dilute hydrochloric acid gives a pale yellow colour, which changes to crimson on boiling.

The crystals of the chloride (A) have been examined by Dr. T. V. Barker, who reports as follows :

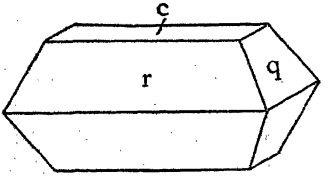
The crystals are orthorhombic (pseudo-tetragonal). The habit is shown in Fig. 2, the list of forms being c (001), r (010), and q (011). The elements $a : b : c = 0{\cdot}998 : 1 : 1{\cdot}828$ were calculated from the following mean results of measurement of three crystals.

	c (001).	q (011).	r (010).
ϕ	Polar.	0° 0′	90° 0′
ρ	Face.	*61 18	*61 21

Optically the crystals are biaxial; birefringence, negative; axial angle, large; dispersion, strong; $\rho < \nu$.

The chloride (A) is very soluble in cold methyl alcohol. When the solution is mixed with methyl-alcoholic potash (25%), an immediate precipitation of potassium chloride occurs; after heating in the water-bath for ½ hour so that much methyl alcohol boils away, the product gives with water a caseous mass which separates from methyl alcohol in prisms, m. p. 125°, and consists of methoxymethyldihydrostrychnidine. The chloride, in quantities of 0·5 g., is cautiously heated in a test-tube over a free flame until effervescence has ceased; the pale yellow, syrupy residue solidifies on cooling, and separates from methyl alcohol in needles, m. p. 202°, which analysis and a mixed m. p. determination prove to be methyl-ψ-strychnidine (p. 1592). This decomposition affords perhaps the most ready method of preparing this substance in a pure condition.

FIG. 2.



*Methyl*neo*strychnidinium Iodide* (B).—The mother-liquors containing sodium iodide from which the iodide (A) originally separated (p. 1611) were concentrated considerably by distillation under reduced pressure, allowed to stand for a couple of days to deposit traces of the iodide (A), and then mixed with aqueous potash (50%) so long as turbidity was produced. After 2 days, the pale salmon, crystalline mass was collected, ground, washed with a little water, and left on porous porcelain to dry. The cake was then dissolved in boiling acetone [in which in this condition it, but not the iodide (A), is rather readily soluble], and the solution was rapidly filtered from the first small crop of crystals and then kept; a copious, colourless, sandy precipitate of the iodide (B) separated which was very sparingly soluble in cold acetone; further crops were

obtained by concentrating the mother-liquor. The iodide (B) begins to darken at 260° and melts and decomposes at about 277° to a black froth (Found: C, 57·3; H, 6·1. $C_{22}H_{27}ON_2I$ requires C, 57·2; H, 5·9%).

This iodide is moderately easily soluble in hot water and separates as a rather indefinite crust on standing; the aqueous solution gives no precipitate with ammonia or caustic potash. It dissolves very readily in warm dilute hydrochloric acid, but exhibits little tendency to crystallise from this solvent.

*Methyl*neo*strychnidinium Chloride* (B).—This was obtained by adding excess of silver chloride to a hot aqueous solution of the iodide (B), heating the mixture on the steam-bath for an hour, and filtering it. The filtrate was concentrated to a small bulk by distillation from the steam-bath under reduced pressure and then left over sulphuric acid in a vacuum desiccator; the pasty mass of minute crystals which gradually formed was left in contact with porous porcelain. The whole residue was dissolved in a very small amount of water, allowed to crystallise again, and transferred to porous porcelain. The colourless residue, dried at 100°, melted at about 255° with effervescence (Found: C, 68·3; H, 7·8. $C_{22}H_{27}ON_2Cl,H_2O$ requires C, 68·0; H, 7·5%). When this chloride is heated with methyl-alcoholic potash under the conditions described in the corresponding case of the chloride (B), a large yield of methoxymethyldihydrostrychnidine, m. p. 125°, is obtained.

In order to determine whether the product of the action of dilute sulphuric acid on methoxymethyldihydrostrychnidine was capable of electrolytic reduction, the solution prepared as explained on p. 1602 was placed in the usual apparatus (p. 1600), and a current of 5 amps. passed for 16 hours at 20°. The solution was then neutralised with ammonia, and a little sulphurous acid added, followed by a large excess of sodium iodide. The bulky precipitate which separated was recrystallised from water and found, by a comparison of properties and an analysis (Found: C, 57·6; H, 6·0. $C_{22}H_{27}ON_2I$ requires C, 57·2; H, 6·0%), to be methyl*neo*strychnidinium iodide (A), showing that reduction had not taken place.

Oxidation of Methyl-ψ-strychnidine. Formation of a Diketone termed Strychnidone.—Methyl-ψ-strychnidine (6 g.), dissolved in warm acetone (400 c.c.), was cooled to 15°, and very finely powdered and sieved permanganate (6 g.) added in small quantities at a time with constant shaking. When decolorisation was complete, the whole was heated on the steam-bath, the manganese precipitate * was

* When this manganese precipitate is extracted with hot water, a dark brown liquid is obtained containing a small quantity of the potassium salt of an acid which has not been obtained crystalline.

filtered off and well washed with acetone, and the combined acetone filtrate and extracts were evaporated on the steam-bath; the syrupy residue soon crystallised and did so immediately when stirred with methyl alcohol. The whole was dissolved in boiling methyl alcohol; from the solution, brilliant, almost colourless prisms separated, and further crops were obtained by concentrating the mother-liquor, the total yield being 5 g. After a second crystallisation from methyl alcohol, the substance was pure (Found: C, 71·3; H, 6·8; N, 8·0. $C_{21}H_{24}O_3N_2$ requires C, 71·6; H, 6·8; N, 7·9%). *Strychnidone* melts at about 152°, is slightly soluble in boiling water, and very sparingly soluble in cold methyl alcohol.

A solution in dilute sulphuric acid gives, with dichromate, a deep crimson colour; ferric chloride added to a solution in dilute hydrochloric acid gives a pale pink colour which becomes crimson on boiling. The powdered crystals dissolve in concentrated nitric acid to a most intense crimson solution, and the colour is not discharged on dilution. The diketone is remarkably resistant to oxidation, the solution even in boiling acetone decolorising permanganate very slowly.

The Disemicarbazone.—The diketo-derivative (2 g.), dissolved in hot dilute acetic acid, was mixed with a concentrated aqueous solution of semicarbazide hydrochloride (5 g.) and sodium acetate (4 g.) and heated on the steam-bath with gradual addition of potassium carbonate so as nearly to neutralise the acetic acid. After 2 hours, the whole was cooled, filtered from a little gum, and made strongly alkaline with ammonia; a chalky precipitate then separated which was well washed, dried on porous porcelain, and then on the steam-bath (Found: C, 58·1; H, 6·7; N, 24·4. $C_{23}H_{30}O_3N_8$ requires C, 59·1; H, 6·4; N, 24·0%). A further crop of this disemicarbazone (Found: N, 24·2%) slowly separated from the aqueous mother-liquor as a definitely crystalline crust, m. p. about 252° (efferv.).

The Oxime.—The diketo-derivative (2 g.) was dissolved in boiling methyl alcohol, a concentrated aqueous solution of hydroxylamine hydrochloride (4 g.) and sodium acetate (5 g.) added, and the whole heated to boiling; the clear solution then gradually became cloudy. After 3 hours, the product was cooled and mixed with water, ammonia was added until the liquid was alkaline, and the precipitate, which was at first syrupy but soon hardened, was ground with water to a paste, washed, and dried over sulphuric acid in a vacuum desiccator (Found: N, 11·1. $C_{21}H_{25}O_3N_3$ requires N, 11·4%). The oxime was very soluble in methyl alcohol; the solution, after addition of much ether, was washed with water, dried over potassium carbonate, and concentrated; the *oxime* then separated in fluffy

masses which had no definite melting point, shrinking at about 150° and effervescing at 170—175° (Found: N, 11·2%). Experiments made with the object of bringing about a Beckmann transformation by means of acetic anhydride or acetyl chloride led to no useful result.

An isomeride of strychnidone was obtained when this substance (6·5 g.), dissolved in the minimum quantity of boiling methyl alcohol, was mixed with methyl-alcoholic potash (25 c.c. of 25%). On heating on the steam-bath, the liquid clouded and a crystalline, chalky precipitate separated. This was collected, washed well with methyl alcohol, and crystallised from much boiling methyl alcohol, from which the substance separated as a colourless, crystalline powder (Found: C, 71·3; H, 7·0; N, 7·7. $C_{21}H_{24}O_3N_2$ requires C, 71·6; H, 6·8; N, 7·9%).

allo-*Strychnidone* shrinks at 245°, gradually becomes brown, and froths at about 260—265°. It dissolves with difficulty in dilute acids and shows the same colour reactions as the original diketo-derivative. It is moderately easily soluble in boiling acetone or xylene and is very stable to permanganate. The same substance appeared to be produced when the original diketo-derivative was left in contact with concentrated sulphuric acid for 2 hours and the brownish-yellow solution, after dilution, was precipitated by ammonia. The decomposing point after recrystallisation was about 265° (Found: C, 71·2; H, 6·9; N, 7·8%). When the methyl-alcoholic solution of the base was boiled with semicarbazide hydrochloride or with hydroxylamine hydrochloride and sodium acetate, under exactly the conditions described above in the case of the isomeride, m. p. 152°, the solution in both cases deposited, on cooling, a mass of crystals of the *allo*-derivative which was identified by the decomposing point, 260°, and by analysis.

Methoxymethylstrychnidonic Acid.—The best conditions for the formation of this substance seem to be the following. Finely powdered methoxymethyldihydrostrychnidine (6 g.), suspended in warm methyl alcohol (50 c.c.), is mixed with methyl-alcoholic potash (10 c.c. of 25%), and perhydrol (20 c.c.) is added all at once. The temperature is kept carefully at 43—44°; a slow effervescence then takes place and a slimy substance separates at first but gradually disappears. After about an hour the effervescence will have ceased. The pale yellow product is left over-night, then mixed with an equal volume of water, and the methyl alcohol removed by distillation under reduced pressure. The filtrate from a small amount of flocculent matter is extracted several times with ether, then with chloroform to remove a gum, which so far has not been investigated, and is again distilled in order to free it from ether and chloroform.

On being acidified with dilute sulphuric acid, the liquid clouds and crude methoxymethylstrychnidonic acid separates as a brown resin. A specimen of the amino-acid in a nearly pure condition was obtained by extracting the crude product with much ether, drying the extract over calcium chloride, distilling off most of the ether, and allowing most of the remainder to evaporate over sulphuric acid; the *amino-acid* then separated as a crust which was not definitely crystalline (Found: C, 64·8; N, 7·5; N, 7·2. $C_{21}H_{28}O_5N_2$ requires C, 65·0; H, 7·2; N, 7·2%).

Anhydromethoxymethylstrychnidonic Acid.—When the crude amino-acid obtained on acidifying the product of the action of perhydrol on methoxymethyldihydrostrychnidine (see above) is warmed with water, almost all dissolves, and on allowing the solution to evaporate at 70—80° it darkens considerably and deposits at first colourless nodules of the anhydro-amino-acid and then a dark tar containing some crystalline matter. The latter is dissolved in a little boiling methyl alcohol and after some days the sparingly soluble anhydro-acid separates as a crust. This is collected and washed with methyl alcohol, the nearly colourless residue mixed with the nodules, and the whole repeatedly crystallised from methyl alcohol (Found: C, 67·6; H, 7·0; N, 7·4; MeO, 8·1. $C_{21}H_{26}O_4N_2$ requires C, 68·1; H, 7·0; N, 7·6; MeO, 8·0%). This anhydro-acid melts at 222° and is sparingly soluble even in boiling methyl alcohol, from which it separates in stars of flat, prismatic needles; on heating in a test-tube, it chars, liberating the odour of indole. It is insoluble in water or cold dilute acids or in dilute caustic soda solution, but dissolves gradually in the last on boiling. The solution in dilute sulphuric acid (60%) gives with dichromate an intense crimson colour, and the solution in warm dilute hydrochloric acid gives with ferric chloride the same coloration. When the anhydro-acid is heated in a sealed tube with methyl iodide and methyl alcohol for a few minutes, a pale yellow solution is obtained which deposits the unchanged anhydro-acid on evaporation.

Ethoxymethyldihydrostrychnidine.—This substance is obtained when powdered strychnidine methosulphate (3 g.) is heated with a saturated solution (25 c.c.) of caustic potash in ethyl alcohol on the steam-bath. The methosulphate gradually dissolves and a cloudy liquid containing drops of oil forms. After 10 minutes, the whole is cooled, water and ice are added, and the chalky precipitate is collected, washed with ice-water, and left on porous porcelain. The substance is very soluble in alcohol; from the solution, after being concentrated and left in the ice-chest, a paste of needles separates which, in contact with porous porcelain, becomes quite colourless but has the tendency, characteristic also of methoxy-

methyldihydrostrychnidine (compare p. 1602), to become purple on exposure to the air. After being dried at 80°, the substance melts at about 98° (Found: C, 75·9; H, 8·4; N, 7·3. $C_{24}H_{32}O_2N_2$ requires C, 75·8; H, 8·4; N, 7·3%). *Ethoxymethyldihydrostrychnidine* is much more readily soluble in solvents than the corresponding methoxy-derivative and exhibits much less tendency to separate in well-defined crystals. It is very soluble in light petroleum and separates from the concentrated solution, on slow evaporation, in hard, lilac-brown prisms.

Methoxymethyltetrahydrostrychnidine.

The corresponding dihydro-derivative (p. 1602) (10 g.), as obtained directly by the addition of water to the product of the action of methyl-alcoholic potash on strychnidine methosulphate, is dissolved in dilute sulphuric acid (150 c.c. of 20%) and reduced, in the apparatus described on p. 1600, by a current of 5 amps. for 15 hours. The product is diluted and mixed with excess of concentrated caustic potash solution, and the solid is collected, dried on porous porcelain, and warmed with a little alcohol to remove traces of gum. The substance is then twice crystallised from xylene, from which it separates very characteristically in well-developed, glistening, short prisms (Found: C, 75·1; H, 8·6; N, 7·5; MeO, 8·1. $C_{23}H_{32}O_2N_2$ requires C, 75·0; H, 8·7; N, 7·6; MeO, 8·3%). *Methoxymethyltetrahydrostrychnidine* melts at 220° and distils at about 230—235°/1 mm. without any decomposition, since the colourless, crystalline distillate melts at 220—222° either alone or mixed with a specimen of the original substance. It is very sparingly soluble in boiling alcohol, and moderately easily soluble in boiling benzene, from which it crystallises well in plates. It dissolves readily in dilute acids. The solution in dilute sulphuric acid gives with dichromate a pink coloration which rapidly changes to reddish-purple. Acetic anhydride appears to be without action, since, after boiling with the anhydride and a drop of sulphuric acid for several minutes, the base was recovered unchanged on addition of ammonia after the acetic anhydride had been decomposed with water.

The *hydriodide* was prepared by dissolving the base in a slight excess of dilute hydrochloric acid, adding a few drops of sulphuric acid, heating the solution to boiling, and mixing it with a large excess of aqueous sodium iodide; from the milky solution thus produced, a gum separated which soon crystallised. The mass was well washed and dissolved in boiling water, and the solution rubbed with a glass rod; a meal of glistening prisms then separated, m. p. 235° (decomp.) (compare p. 1623) (Found: C, 56·0; H, 6·7. $C_{23}H_{32}O_2N_2$,HI requires C, 55·7; H, 6·7%). This hydriodide is

very sparingly soluble in boiling methyl alcohol and separates well, on cooling, in small, colourless needles. Its conversion into methyl-*neo*dihydrostrychnidinium iodide by the action of heat is described on p. 1623.

The Methiodide (*a*), $C_{23}H_{32}O_2N_2$,MeI.—The base, m. p. 220°, does not combine readily with methyl iodide and may indeed be recrystallised from methyl iodide without change. In an experiment in which the base was boiled with methyl alcohol and a large excess of methyl iodide for 12 hours, the clear solution, on being concentrated, deposited a large amount of the unchanged base. When, however, the powdered base (2·5 g.) was heated with methyl iodide (8 c.c.) in a sealed tube in the steam-bath for 5 hours, complete solution gradually took place and, on cooling, a mass of crystals separated, or in some experiments a syrup formed on the surface of the methyl iodide which became crystalline on being rubbed with methyl alcohol. In either case, the crystals were collected, washed with methyl iodide, and recrystallised from a little boiling alcohol, from which the *methiodide* separated, on slowly cooling, as a glistening crust of arrow-shaped prisms (Found: C, 56·0; H, 7·0; I, 24·5. $C_{24}H_{35}O_2N_2I$ requires C, 56·4; H, 6·9; I, 24·9%). This methiodide melts at about 227° with vigorous effervescence. In order to determine the nature of this decomposition, about a gram of the substance was heated in a test-tube at 250°; methyl iodide then condensed on the cold part of the tube. After effervescence had ceased, the nearly colourless gum was dissolved in much boiling methyl alcohol, and the solution concentrated; on cooling, methoxymethyltetrahydrostrychnidine separated in prisms, m. p. 220°. The methiodide is decomposed with great difficulty by methyl-alcoholic potash, since, after boiling for several minutes, most of the unchanged methiodide is recovered on the addition of water. The methyl iodide washings of the crude methiodide gave a syrup on evaporation; a solution of this in boiling methyl alcohol, on standing exposed to air, deposited thick prisms of methoxymethyltetrahydrostrychnidine, showing again the small tendency this base has to combine with methyl iodide.

The Methochloride (*a*).—This was prepared by warming the methiodide with water and excess of silver chloride on the steam-bath for 2 hours and then evaporating the filtrate from the silver salts; the methochloride separated as a waxy, crystalline mass, which was not analysed. When this substance was heated on the steam-bath with excess of methyl-alcoholic potash (20%), decomposition took place immediately with separation of potassium chloride, and, as the product was completely soluble in water, it is probable that the methohydroxide was present at this stage.

If, instead of diluting the mixture with water, the whole is heated at 140° until nearly all the methyl alcohol has evaporated, a crystalline precipitate of methoxymethyltetrahydrostrychnidine is obtained on the addition of water.

The Dimethosulphates, $C_{23}H_{32}O_2N_2,2Me_2SO_4$ (A) *and* (B).—Methoxymethyltetrahydrostrychnidine does not combine readily with methyl sulphate, as is shown by the fact that, if methyl sulphate is added to a boiling concentrated solution of the base in benzene, the unchanged substance crystallises on cooling. Combination takes place readily, however, under the following conditions and with the formation of the dimethosulphates. The base (8 g.), dissolved in specially purified and dried benzene (100 c.c.), is mixed with carefully purified methyl sulphate (20 c.c.) and boiled under reflux with exclusion of moisture; in about 2 hours, the liquid begins to cloud and a gelatinous mass to separate. The boiling is continued for 20 hours, and the hot benzene then decanted from the gummy mass. After several days, the benzene solution deposits a soft, crystalline crust, which is washed with benzene and dried over sulphuric acid in a vacuum desiccator (Found: C, 51·8; H, 6·9. $C_{23}H_{32}O_2N_2,2Me_2SO_4$ requires C, 52·2; H, 7·1%). That this substance is the *dimethosulphate* (A) was confirmed by the fact that the solution in boiling methyl alcohol gave, on the addition of sodium iodide and cooling, the dimethiodide (A), m. p. 315—320° (decomp.). In preparing this substance in quantity, the horny mass of dimethosulphate from which the benzene had been decanted was dissolved in warm water, and the solution was filtered from benzene and mixed with a considerable excess of hot concentrated sodium iodide; the clear solution, on rubbing, immediately began to deposit the *dimethiodide* (A) in flat prisms. After some hours, the crystalline mass was collected, well washed, and dried on porous porcelain and then on the steam-bath (Found: C, 45·8; H, 5·6. $C_{23}H_{32}O_2N_2,2MeI$ requires C, 46·0; H, 5·8%). This dimethiodide (A) does not discolour until 300° and melts and effervesces at about 315° to a reddish-brown froth. It dissolves readily in boiling water and separates on cooling in needles; in boiling methyl alcohol it is very sparingly soluble, but it dissolves in much boiling ethyl alcohol and separates on slow cooling in striated, quadrilateral plates.

The Dimethochloride (A).—A boiling aqueous solution of the dimethiodide (A) was readily decomposed by silver chloride and, on evaporating the filtrate from the silver salts to a small bulk and leaving it over sulphuric acid, a gummy mass was obtained which gradually crystallised but was not analysed. The solution in dilute sulphuric acid gives with dichromate a pink coloration which becomes crimson on warming. The conversion of this dimethoc

chloride (A) into methyl-ψ-dihydrostrychnidine, $C_{22}H_{28}ON_2$, by the action of heat is described on p. 1621.

Methoxymethyltetrahydrostrychnidine Dimethiodide (B), $C_{23}H_{32}O_2N_2,2MeI$.—When the solution of the dimethosulphate, prepared as described on p. 1619, was treated with sodium iodide, less than half the calculated amount of the dimethiodide (A) separated, and very little more was obtained on standing or concentration. On investigating the cause of this, it was found that the addition of caustic potash solution (50%) to the mother-liquor of (A) produced a heavy caseous precipitate. After alkali had been added until there was no further separation, the whole was warmed at 50°; the precipitate then melted and settled on the bottom of the beaker as a viscid gum. The supernatant alkaline solution was decanted, the syrup dissolved in boiling methyl alcohol, and the solution filtered and concentrated; on standing, a thick mass of colourless prisms gradually separated, and more was obtained by concentrating the mother-liquor. This dimethiodide (B) is very readily soluble in boiling methyl alcohol, but sparingly soluble in the cold, and separates in thick, four-sided, twin prisms which effervesce at about 165° owing to the escape of methyl iodide (see below) (Found: C, 46·7; H, 5·9. $C_{25}H_{38}O_2N_2I_2$ requires C, 46·0; H, 5·8%). The final methyl-alcoholic mother-liquors, from which no more of the dimethiodide (B) could be separated, on being concentrated and kept for months in the air, yielded a semi-solid paste; this, in contact with porous porcelain, gradually left a white, crystalline mass, a solution of which in methyl alcohol, when allowed to concentrate in the air, gradually deposited large, glistening prisms, m. p. 225° (vig. efferv.) (Found: C, 56·2; H, 7·0. $C_{23}H_{32}O_2N_2,MeI$ requires C, 56·4; H, 6·8%). Since this substance decomposed on heating into methyl iodide and methoxymethyltetrahydrostrychnidine, it is evident that it was the methiodide of this substance described on p. 1618, and its formation shows that the crude dimethosulphate prepared in benzene solution with a large excess of methyl sulphate contains some monomethosulphate in spite of the fact that a very large excess of methyl sulphate was used and the heating continued for 20 hours (p. 1619).

Methoxymethyltetrahydrostrychnidine Methiodide (*b*).—When the dimethiodide (B) just described is heated in a test-tube in a bath at about 220°, methyl iodide is eliminated and condenses on the cold sides of the tube. In a quantitative experiment, 0·2440 g., heated at 165°, rising to 230° until decomposition was complete, lost 0·1047 g. or 42·8%, whereas $C_{23}H_{32}O_2N_2,2MeI$ losing 2MeI requires a loss of 43·5%. On crystallising the residue from alcohol, colourless leaflets separated which melted at 220° and consisted of methoxy-

methyltetrahydrostrychnidine (Found: C, 74·9; H, 8·6. Calc. for $C_{23}H_{32}O_2N_2$: C, 75·0; H, 8·7%). The elimination of only 1 mol. of methyl iodide was accomplished under the following conditions. The dimethiodide (B) was gently boiled in a test-tube with carefully dried mesitylene; it then became spongy and granular but did not dissolve. The crystalline deposit was collected, washed with warm mesitylene, and crystallised from a large volume of methyl alcohol, in which it was very sparingly soluble and from which it separated as a sandy, crystalline powder (Found: C, 55·8; H, 6·7. $C_{23}H_{32}O_2N_2$,MeI requires C, 56·4; H, 6·9%). This methiodide (*b*) becomes brown at 300—320°, decomposes with effervescence at about 325° into methyl iodide and methoxymethyltetrahydrostrychnidine, and is readily soluble in boiling water. It is therefore isomeric with the methiodide (*a*) described on p. 1618, which melts at 227°, and it is interesting that both these isomerides lose methyl iodide on heating and yield methoxymethyltetrahydrostrychnidine.

Methoxymethyltetrahydrostrychnidine Dimethochloride (B).—The pure dimethiodide (B), m. p. 165°, was treated with water and silver chloride on the steam-bath in the usual way; the filtrate from the silver salts was evaporated to a small bulk on the steam-bath and then left over sulphuric acid in a vacuum desiccator, but there was no sign of crystallisation and the whole dried to a horny mass. This became brittle on the steam-bath and could be powdered, but the powder rapidly absorbed moisture and became sticky. When the dry substance was heated in a test-tube in a sulphuric acid bath, methyl chloride was eliminated; the effervescence being over, the residue was crystallised from xylene, colourless prisms being thus obtained which melted at 220—222° and consisted of methoxymethyltetrahydrostrychnidine [compare the action of heat on the dimethochloride (A),; see below].

Methyl-ψ-dihydrostrychnidine, $C_{22}H_{28}ON_2$.—This substance is obtained from the dimethochloride (A) of methoxymethyltetrahydrostrychnidine (p. 1619) or from methyl*neo*dihydrostrychnidinium chloride (p. 1623) by heating. The dimethochloride (A), in quantities of not more than 0·5 g., is cautiously heated in test-tubes over a free flame; it soon gives off steam and doubtless also methyl alcohol and then froths at a very high temperature, giving a very unpleasant smelling vapour, which burns with a smoky flame tinged with green, and a small amount of a colourless, crystalline sublimate forms on the sides of the tube. When the effervescence has ceased, the ochre-coloured residue, which crystallises on cooling, is dissolved in much boiling methyl alcohol; the solution, on being concentrated considerably and left in the ice-chest, deposits the new substance in colourless spangles, but the yield is poor even after the mother-

liquors have been worked up (Found: C, 78·1; H, 8·0; N, 8·5. $C_{22}H_{28}ON_2$ requires C, 78·6; H, 8·3; N, 8·3%).

Methyl-ψ-dihydrostrychnidine melts at 212° and is somewhat soluble in boiling water to a bitter solution which, on cooling, deposits the substance in flitters. It is sparingly soluble in cold methyl alcohol and very sparingly soluble in acetone even on boiling; it separates from the solution, on concentration, in glistening, colourless plates. It is also sparingly soluble in benzene or light petroleum. The solution in acetone does not decolorise permanganate except on the addition of a little water and then only on long standing. The resistance to oxidation was shown in an experiment in which the base (1 g.), dissolved in much boiling acetone and water (3 c.c.), was boiled under reflux, and permanganate (1·5 g.) gradually added. After some hours, decoloration was complete and the acetone filtrate from the manganese precipitate yielded, on being concentrated, 0·7 g. of unchanged substance. A solution of the base in dilute sulphuric acid gives with dichromate a yellow solution which becomes crimson on warming; a solution in dilute hydrochloric acid is coloured yellowish-pink by ferric chloride, the colour changing to crimson on warming. The base dissolves with effervescence in concentrated nitric acid to a reddish-brown solution.

The Methiodide, $C_{22}H_{28}ON_2$,MeI.—When the base, m. p. 212°, was mixed with methyl iodide, there was some rise of temperature. The chalky precipitate produced after the mixture had been heated in a sealed tube for 15 minutes was crystallised from methyl alcohol, in which it was very sparingly soluble and from which it separated in glistening groups of slender needles (Found: C, 57·6; H, 6·3. $C_{23}H_{31}ON_2I$ requires C, 57·7; H, 6·4%). This methiodide is very sparingly soluble in boiling water. It becomes brown at 290° and decomposes with effervescence at about 330—335° to a brown syrup, which crystallises on cooling; this decomposition product was not further investigated.

The *methochloride*, prepared in the usual manner by boiling the methiodide with water and silver chloride, separated from the concentrated aqueous solution, on standing over sulphuric acid, in colourless, very readily soluble needles and was not analysed. It darkens at 260° and effervesces at about 315° to a black syrup. The solution in dilute sulphuric acid gives with permanganate a pink coloration which becomes an intense crimson on standing or warming.

*The Methyl*neo*dihydrostrychnidinium Salts.*

Methoxymethyltetrahydrostrychnidine, unlike the corresponding dihydro-derivative (p. 1610), is not acted on by boiling dilute sulphuric

acid: the tetrahydro-base (5 g.) was boiled with sulphuric acid (20% by vol.) for 3 hours, but there was no sign of any elimination of methyl alcohol and on addition of ammonia a caseous precipitate separated which was found to be the unchanged base, practically the whole being recovered. The only way in which the methyl*neo*-dihydrostrychnidinium salts could be prepared was from methoxymethyltetrahydrostrychnidine hydriodide (p. 1617) by the action of heat. The air-dried substance, in quantities of 0·5 g., was spread evenly over the lower surface of large test-tubes and these were heated by a sulphuric acid bath gradually to 230° and kept at this temperature for about 3 minutes; the vapours which came off during the decomposition were apparently water and methyl alcohol. After effervescence had ceased, the residual syrup crystallised, on cooling, as a hard, pale brown crust. This was very sparingly soluble in boiling water, but dissolved very readily in warm dilute hydrochloric acid (compare p. 1611). The solution, after being decolorised with norite, was mixed with excess of ammonia, left for 24 hours, filtered from a small, fluffy, brown precipitate, and concentrated on the steam-bath to a small bulk. The solution of ammonium chloride was decanted from the sparingly soluble, brown crusts which had separated, and the crusts were dissolved in much boiling water. On concentrating the solution considerably, the iodide separated in well-developed, pale brown prisms (Found: C, 57·2; H, 6·4. $C_{22}H_{29}ON_2I$ requires C, 56·9; H, 6·3%).

*Methyl*neo*dihydrostrychnidinium iodide* melts at about 350° with effervescence and is sparingly soluble in alcohol, xylene, or glacial acetic acid. This iodide was rubbed into a paste with hot water and heated on the steam-bath for 2 hours with excess of silver chloride. The filtrate from the silver salts was evaporated to a small bulk and the solution placed over sulphuric acid in a vacuum desiccator; a paste of crystals then formed. In contact with porous porcelain, the mother-liquor was readily absorbed, leaving a hard, colourless mass of *methyl*neo*dihydrostrychnidinium chloride* (Found in material dried at 100°: C, 70·7; H, 8·1. $C_{22}H_{29}ON_2Cl$ requires C, 70·8; H, 7·9%). This chloride is very readily soluble in water. The solution in dilute sulphuric acid gives with dichromate an intense crimson coloration in the cold. The dry substance changes colour at 300° and decomposes at about 345° with effervescence, leaving a brown syrup. In investigating this change, the dry substance (0·5 g.) was very cautiously heated in a large test-tube by a free flame until effervescence had ceased; during this decomposition a very pungent and unpleasant smelling vapour was given off which tinged a flame green. The brown syrup solidified, on cooling, to a very hard crust. A solution of this in much boiling

methyl alcohol was decolorised by boiling with norite for an hour and then concentrated; a mass of colourless plates then gradually separated which melted at 210—212° and consisted of methyl-ψ-dihydrostrychnidine, as a comparison of properties and a mixed melting point demonstrated. This is probably the most convenient method of preparing this base, but the yield in this case also is not good.

Methylstrychnine.—This substance may be quickly and conveniently prepared in good yield by the following process. Strychnine (100 g.), finely powdered and passed through a 40-mesh sieve, is stirred in a mortar with the gradual addition of pure methyl sulphate (68 c.c.); the whole soon sets to a solid mass of strychnine methosulphate. This is broken up, left over-night, and dissolved in warm water (300 c.c.), the solution is filtered from unchanged methyl sulphate (about 2 c.c.), and then caustic potash (170 c.c. of 50%) added with shaking. Crystallisation soon sets in and after remaining over-night the crystals are collected and dissolved in boiling water (260 c.c.), and the solution is filtered from unchanged strychnine (about 2 g.) and allowed to cool; the stout, colourless prisms of methylstrychnine, $C_{22}H_{24}O_2N_2,4H_2O$, that separate are collected and dried on the steam-bath. The colourless powder (93 g.) melts and decomposes at about 318—320°. The aqueous mother-liquors are used for the recrystallisation of another batch of crude methylstrychnine.

Normethylstrychnine.—When methylstrychnine, powdered and dried on the steam-bath, is heated in a distilling flask under 1 mm. by a metal bath kept at 200—205°, it gradually melts, there is much effervescence and some sublimation, and the loss is about 15%. The heating is continued for about ½ hour, and the residual resin is then dissolved in a slight excess of dilute hydrochloric acid, ammonia is added until there is a slight precipitation, and the filtered solution is mixed with excess of ammonia and warmed at 50° on the steam-bath. The pale brown, granular precipitate is collected and dissolved in excess of warm oxalic acid; after 2 days, a small amount of a dark crust separates. The filtrate from this is vigorously shaken while dilute ammonia is carefully added so long as a dark-coloured precipitate forms. After being filtered, the solution is shaken with norite and filtered, and excess of ammonia is added to the pale yellow filtrate. A voluminous, pale ochre precipitate separates which becomes granular on warming at 50°, and this is collected, washed, and dried over sulphuric acid in a vacuum desiccator (Found in two different preparations: C, 75·7 and 75·2; H, 6·8 and 6·7; N, 8·2. $C_{21}H_{22}O_2N_2$ requires C, 75·4; H, 6·6; N, 8·4%). This base, which is isomeric with strychnine, has so far

not been obtained in a crystalline condition. A solution in dilute sulphuric acid (60% by vol.) gives with dichromate an intense bluish-purple colour, fading to a port wine tint; a solution in dilute hydrochloric acid gives with ferric chloride no coloration in the cold and there is little change on warming.

The Methiodide.—The base was heated in a sealed tube in the steam-bath with a large excess of methyl iodide for 5 hours. Next day, the crust of prisms which had separated on the sides of the tube was scraped off, washed with methyl iodide, and dried on the steam-bath. The old-gold, crystalline mass became opaque at 180°, darkened at 290°, and frothed at about 315° (Found: C, 54·9; H, 5·5. $C_{21}H_{22}O_2N_2$,MeI requires C, 55·4; H, 5·3%). This methiodide of normethylstrychnine was digested with water and silver chloride on the steam-bath, and the pale green filtrate concentrated to a small bulk; a soft, satiny mass separated on standing. This became colourless on porous porcelain and melted at about 285° (Found: C, 68·9; H, 6·6; N, 7·2. $C_{21}H_{22}O_2N_2$,MeCl requires C, 68·7; H, 6·5; N, 7·3%). A solution of this methochloride in dilute sulphuric acid (60% by vol.) gives with dichromate an intense indigo-blue colour, fading to brown. Methylstrychnine (10 g.) mixed with phenol (15 g.) was heated at 240° for an hour; the distillate, on treatment with dilute potash, yielded anisole (1·2 g.), which was recognised by its boiling point and other properties.

Action of Caustic Potash on Methylstrychnine.—Methylstrychnine (10 g.), mixed with methyl-alcoholic potash (60 c.c. of 20%), was heated on the steam-bath for 15 minutes with stirring, powdered potash (30 g.) was then added, and the decomposition continued at 150—200° for 20 minutes with frequent stirring; the temperature was then raised to 250° for 30 minutes. The product from five such operations was steam-distilled, the oil that passed over was extracted with ether, and the extract was dried over potassium carbonate and fractionated. The portion that distilled between 148° and 155°/15 mm., on remaining in the ice-chest, deposited crystals which were collected, drained on porous porcelain, and recrystallised from petroleum. The colourless plates thus obtained in considerable quantity melted at 52° and consisted of indole, as a mixed melting-point determination and a careful comparison of properties conclusively proved. The reddish-brown solution in the steam-distillation flask was cooled, sulphur dioxide passed in, and the precipitate collected, dried, and distilled in quantities of 3 g. with soda-lime under reduced pressure. The distillate, containing oily drops, was extracted with ether, and the extract steam-distilled; a further quantity of indole then passed over. Finally, the residue in the steam-distillation flask was extracted with benzene and distilled,

and the fraction, b. p. 240—280°/16 mm., was dissolved in low-boiling petroleum; from the solution a pasty mass of crystals separated which, after recrystallisation, melted at 236°, and this substance was found, by an examination of its colour reactions and other properties and by a mixed m. p. determination, to be carbazole.

Decomposition by soda-lime. Methylstrychnine (2·5 g.) was mixed with soda-lime (10 g.) and heated in a hard glass tube under 20 mm. to about 400°. The distillate from several such operations was steam-distilled, the pale yellow oil extracted with ether, and the extract dried over potassium carbonate and fractionated; an oil passed over at 93°/25 mm. which was insoluble in dilute hydrochloric acid, gave an intense purple colour with *p*-dimethylaminobenzaldehyde, and yielded a picrate, m. p. 168°. The amount obtained was too small to allow of its constitution being determined.

The residue from the steam distillation yielded a small amount of a substance which separated from light petroleum in glistening plates, m. p. 236°, and was recognised as carbazole.

Electrolytic Reduction of Methylstrychnine.—Methylstrychnine (20 g.), dissolved in dilute sulphuric acid (100 c.c. of 60%), was reduced in the usual apparatus (p. 1600) by a current of 5 amps. for 16 hours, the pale pink solution diluted with water and heated on the steam-bath, and barium carbonate added until the sulphuric acid had been removed. The strongly alkaline solution from the barium sulphate was evaporated to dryness; the almost colourless, crystalline methylstrychnidinium hydrogen carbonate that remained was purified by dissolving it in methyl alcohol, in which it was readily soluble, and fractionally precipitating it with ether. The second fraction, after drying on porous porcelain over sulphuric acid in a vacuum desiccator, gave analytical results agreeing approximately with those required for the formula

$$C_{22}H_{27}ON_2,HCO_3,H_2O$$

(Found: C, 65·8; H, 6·9; N, 6·8. Calc.: C, 66·6; H, 7·2; N, 6·8%). When this carbonate was heated at 100° it lost 4·4% (Calc., 4·3%) (Found: C, 69·0; H, 7·4; N, 7·0. $C_{23}H_{28}O_4N_2$ requires C, 69·7; H, 7·1; N, 7·1%). This carbonate is readily soluble in hot water and effervesces with acids; the dry substance also effervesces, when it is heated at 200°, with formation of a colourless syrup. It was readily soluble in hot methyl-alcoholic potash (25%), and after heating in an open flask on the steam-bath for 15 minutes so that considerable concentration had taken place, the milky liquid gave, on dilution with water, a caseous precipitate which separated from methyl alcohol in glistening prisms, m. p. 124—125°, and proved to be methoxymethyldihydrostrychnidine (Found: C, 75·0; H,

8·2. Calc. for $C_{23}H_{30}O_2N_2$: C, 75·4; H, 8·2%). When the carbonate was treated with hydrochloric acid, it yielded a horny methochloride which appeared to be identical with the substance obtained from strychnidine methiodide by treatment with silver chloride (p. 1601).

UNIVERSITIES OF OXFORD AND MANCHESTER.

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CCXI.—*Strychnine and Brucine. Part V.*

By JOHN MASSON GULLAND, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

THE present communication contains the description of part of a general investigation of the reduction products of brucine, our knowledge of which is comparatively scanty. Reduction by hydrogen in presence of colloidal palladium yields dihydrobrucine (Skita and Franck, *Ber.*, 1911, **44**, 2864), and Tafel and Naumann (*Ber.*, 1901, **34**, 3291) have described the preparation by electrolytic reduction of a substance which they designate "tetrahydrobrucine."

The starting point of the research now to be described is brucidine, a substance which Tafel and Naumann (*loc. cit.*) claim to have prepared from "tetrahydrobrucine" by the elimination of water at 215°. The two substances were thus considered to be analogous to tetrahydrostrychnine and strychnidine and were represented by the scheme:.

$$(MeO)_2(C_{20}H_{20}O)(:N)\leqslant^{CH_2\cdot OH}_{NH} \longrightarrow (MeO)_2(C_{20}H_{20}O)(:N)\leqslant^{CH_2}_{N}$$

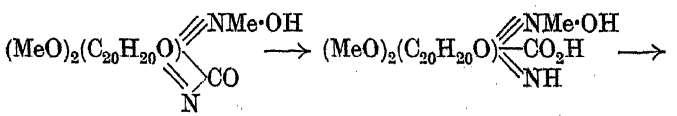
Tetrahydrobrucine. *Brucidine.*

The properties of these substances as described by Tafel are extremely similar, and he was unable to demonstrate by the preparation of a nitrosoamine the presence of an imino-group in the secondary amine, tetrahydrobrucine. We have repeated the electrolytic reduction of brucine, using the modified apparatus described in a previous communication (J., 1924, **125**, 1798), and our results show that Tafel's "tetrahydrobrucine," m. p. 200—201°, should be re-named brucidine. It is clear, however, that his "brucidine," m. p. 198°, was correctly named, although it was not quite homogeneous and was identical with his supposed "tetrahydrobrucine." We have now obtained two products, (i) *brucidine*, m. p. 203—203·5°, which shows all the properties of Tafel's "tetrahydrobrucine," and (ii) *tetrahydrobrucine*, m. p. 177°, which is a secondary amine yielding a *nitrosoamine*. The second substance, moreover, yields brucidine when dehydrated by means of phosphorus

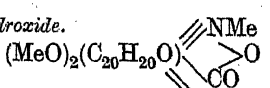
oxychloride, and the two compounds are thus entirely analogous to the corresponding derivatives of strychnine. Tafel's analyses of " tetrahydrobrucine " are in agreement with the theory for brucidine containing a molecule of methyl alcohol, and we have found that the base when crystallised from methyl alcohol does in fact retain one molecule of the solvent.

Tetrahydrobrucine and brucidine are di-acid bases each of which forms a *dihydrochloride* and a *dihydriodide*, but only a monomethiodide when heated with an excess of methyl iodide in boiling methyl alcohol.

The starting materials in the experiments described in this communication are the brucidine metho-salts, and of these the *methosulphate*, prepared by the direct combination of the base with methyl sulphate, is the most easily obtained in practice. Brucidine metho-salts, however, have also been prepared by the electrolytic reduction of methylbrucine. This substance was first obtained (Moufang and Tafel, *Annalen*, 1899, **304**, 42) by the decomposition of brucine methiodide with silver sulphate, followed by the removal of the sulphuric acid by baryta, and Tafel represented it as a betaine according to the scheme :



Brucine methohydroxide.



Methylbrucine.

Leuchs and Anderson (*Ber.*, 1911, **44**, 3046), however, prepared this compound more simply by the action of sodium hydroxide on brucine methosulphate, and we have employed a slight modification of their method. The electrolytic reduction of methylbrucine in dilute sulphuric acid is followed by the removal of the sulphuric acid by means of barium carbonate. In this way, *brucidine methohydrogencarbonate* is obtained, and from it may be prepared *brucidine methohydroxide* by the action of alkali, and also *brucidine methiodide* by means of sodium iodide. This methiodide is identical with a specimen prepared by the interaction of the base with methyl iodide, and it is therefore evident that the nitrogen atom which is involved in the production of brucidine metho-salts is not that which forms part of the group $-CO-N:$ of brucine.

When brucidine methochloride or methosulphate,

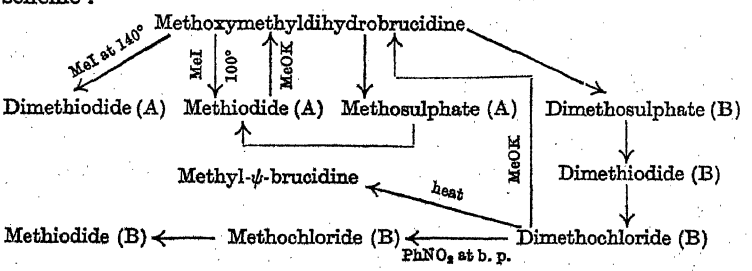
$$C_{22}H_{28}O_3N_2,Me_2SO_4,$$

is digested with methyl-alcoholic potassium hydroxide it is converted into *methoxymethyldihydrobrucidine*, $C_{25}H_{34}O_4N_2$, m. p. 115°, which is derived from brucidine by the introduction of a methyl group and the addition of methyl alcohol. Unlike the corresponding derivative of strychnidine, this substance is a di-acid base, yielding a *dihydriodide*, but here, as in the case of brucidine, one molecule only of methyl iodide enters easily into combination with the base. The formation of this *methiodide* (A) by the action of methyl iodide at 100° takes place smoothly in the absence of a solvent, but when methyl alcohol is employed in the preparation, a small quantity of *oxymethoxymethyldihydrobrucidine*, $C_{25}H_{34}O_5N_2$, m. p. 277°, is produced, and a little of the same substance may be isolated from the mother-liquors when the methiodide, prepared in the absence of a solvent, is recrystallised from methyl alcohol. By far the greater proportion of the product of the action of methyl iodide on methoxymethyldihydrobrucidine under either set of conditions is the methiodide (A), and in this the brucidine derivative differs greatly from the parallel strychnidine one (compare this vol., p. 1591). Indications have been obtained of the formation in these reactions of a second iodine-free *base*, melting at about 218°, which may correspond to oxymethoxymethyldihydrostrychnidine (A), but this substance has not been obtained in a pure condition, because recrystallisation from methyl alcohol converts it into oxymethoxymethyldihydrobrucidine, m. p. 277°. Oxymethoxymethyldihydrobrucidine is probably formed by an atmospheric oxidation which is catalysed by small quantities of iodine, since it has recently been obtained in much greater yield when an ethyl-alcoholic solution of methoxymethyldihydrobrucidine containing a few small crystals of iodine is exposed to the air for some days. A parallel experiment in which the iodine was omitted yielded no oxymethoxymethyldihydrobrucidine in the same space of time.

Further atmospheric oxidation takes place in boiling methyl-alcoholic solution, and a *dioxymethoxymethyldihydrobrucidine* (X), $C_{25}H_{34}O_6N_2$, m. p. 270°, has been isolated. This substance is isomeric with two *dioxymethoxymethyldihydrobrucidines*, namely (Y) and (Z) (p. 1631), which are produced by oxidation of methoxymethyldihydrobrucidine by permanganate. The investigation into the constitution of these substances, their relationship, and the significance of their formation has not yet been completed.

Methoxymethyldihydrobrucidine combines readily at 100° with one molecule of methyl iodide, as has been stated above, but when the temperature is raised to 140° and the reaction prolonged for some hours, the *dimethiodide* (A), m. p. 215°, is formed. In a similar way, methoxymethyldihydrobrucidine reacts slowly with methyl

sulphate at 100° to form the *monomethosulphate* (A), but if the reaction is continued for a day the base is converted quantitatively into the *dimethosulphate* (B). This substance has not been obtained in a crystalline form, but when sodium iodide is added to its aqueous solution the *dimethiodide* (B), m. p. 290°, is precipitated and easily obtained in a pure condition. The *dimethochloride* (B), prepared from the dimethiodide by the action of silver chloride, is a horny mass which has been decomposed in three different ways. When boiled with methyl-alcoholic potassium hydroxide, it loses two molecules of methyl chloride, and methoxymethyldihydrobrucidine is regenerated. When the dimethochloride is heated for a short time in boiling nitrobenzene, the chief product is *methoxymethyldihydrobrucidine methochloride* (B), produced by the liberation of one molecule of methyl chloride. Sodium iodide converts this substance into the *methiodide* (B), which is isomeric with the methiodide (A) mentioned above. When, thirdly, the dry dimethochloride (B) is heated, it loses two molecules of methyl chloride and one of methyl alcohol and yields *methyl-ψ-brucidine* (p. 1631). It will be observed that methoxymethyldihydrobrucidine not only forms two series of metho-salts, depending probably upon which of the two nitrogen atoms is involved, but also two series of dimetho-salts, which are probably stereoisomeric. The relationships existing in this complex group of substances are readily understood from the following scheme:



A consideration of the colour reactions of the reduced brucidine derivatives, especially that given with ferric chloride (see p. 1661), leads to the conclusion that the methiodide (A) has the formula $(MeO)_2(C_{20}H_{20}O)(OMe)(:NMe)\left\langle \begin{matrix} CH_2 \\ | \\ NMe \end{matrix} \right\rangle I$, whilst the methiodide (B) is $(MeO)_2(C_{20}H_{20}O)(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ | \\ N \end{matrix} \right\rangle I$. This is noteworthy and implies that the more basic of the two nitrogen atoms of brucidine becomes the less basic of the two nitrogen atoms of methoxymethyldihydrobrucidine.

Dilute nitric acid has apparently little oxidising action on

methoxymethyldihydrobrucidine, as this reagent at 100° yields only *nitromethoxymethyldihydrobrucidine*, $C_{25}H_{33}O_6N_3$. When, however, the oxidation is brought about by means of potassium permanganate in acetone, two isomeric *dioxymethoxymethyldihydrobrucidines*, $C_{25}H_{34}O_6N_2$, are produced, namely (Y), m. p. 185—186°, and (Z), m. p. 110—111°. The first of these substances (Y) is a base and yields a *methiodide*, which has the interesting property of existing simultaneously in two interconvertible forms; one contains solvent of crystallisation, the other does not. This base is not altered by boiling for a short time with acetic anhydride, and attempts to form a semicarbazone resulted in a dark red, uncrystallisable oil. The second substance (Z) shows more feebly basic properties, since, although it is readily soluble in dilute hydrochloric acid, it does not react with methyl iodide at 100°.

In order to determine whether a process similar to the formation of methoxymethyldihydrobrucidine would occur if ethyl alcohol were substituted for the methyl alcohol used in the preparation of this substance, brucidine methosulphate was digested with sodium ethoxide in ethyl alcohol. A sandy powder was obtained which showed no tendency to crystallise, and was therefore analysed in the form of its crystalline methiodide. This proved to be *ethoxymethyldihydrobrucidine methiodide*, $C_{26}H_{36}O_4N_2,MeI$. The reaction thus follows a course similar to that observed when methyl alcohol is used, but the product was not further investigated.

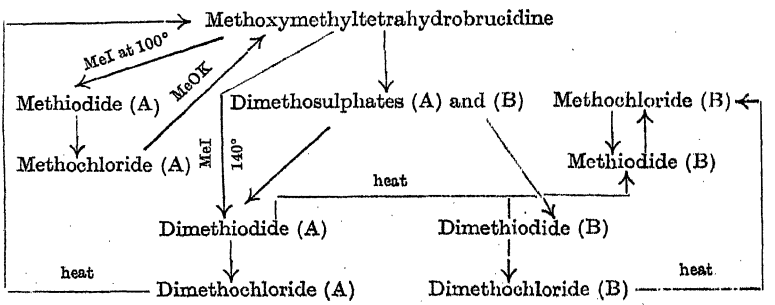
When methoxymethyldihydrobrucidine is boiled with dilute sulphuric acid, methyl alcohol is eliminated, and as no precipitate is formed on the addition of ammonia or sodium hydroxide the solution evidently contains a quaternary sulphate. On addition of an excess of sodium iodide *methyl*neo*brucidinium iodide*, $C_{24}H_{31}O_3N_2I$, m. p. 298°, is precipitated, and the investigation of the mother-liquors yielded only a further quantity of the same iodide. It would thus appear that, in contrast to the behaviour of methoxymethyldihydrostrychnidine under similar conditions (this vol., p. 1593), only one iodide is formed, which, it should be noted, is isomeric with brucidine methiodide, m. p. 322°. *Methyl*neo*brucidinium chloride*, prepared from the iodide by means of silver chloride, may be decomposed in two ways. When digested with methyl-alcoholic potassium hydroxide, it gains methyl alcohol and loses hydrogen chloride, forming methoxymethyldihydrobrucidine. On the other hand, if the dry chloride is heated it loses hydrogen chloride, forming *methyl-ψ-brucidine*.

Methyl-ψ-brucidine, $C_{24}H_{30}O_3N_2$, m. p. 198—199°, is obtained either in the manner described above, or by heating methoxymethyldihydrobrucidine dimethochloride (B). It is a base, forming a

dihydriodide, but only a *methiodide* when combined directly with methyl iodide in the cold. Small quantities of the base and also of its methochloride are formed during the decomposition of methoxymethyldihydrobrucidine dimethochloride (B) in boiling nitrobenzene; the methochloride, which was not isolated, yields the above-mentioned methiodide when treated with sodium iodide. Methyl-ψ-brucidine is unchanged by electrolytic reduction or by shaking in an atmosphere of hydrogen in presence of colloidal palladium, but it is readily oxidised by potassium permanganate to brucidone, $C_{23}H_{28}O_5N_2$, one atom of carbon being lost during the process. This most interesting substance, the analogue of strychnidone, is unfortunately an oil, but a crystalline *monosemicarbazone* was obtained and analysed. The stability of methyl-ψ-brucidine towards reducing agents is noteworthy and cannot, at present, be explained.

Methoxymethyltetrahydrobrucidine, $C_{25}H_{36}O_4N_2$, m. p. 133—135°, is derived from methoxymethyldihydrobrucidine by electrolytic reduction. It is characterised by the facility with which it crystallises, and also shows greater stability to light and air than the methoxydihydro-derivative. It is a di-acid base yielding a *dihydrochloride* and a *dihydriodide*, and like the methoxydihydro-derivatives it forms two series of metho-salts, namely (A) and (B), and also two series of dimetho-salts, namely (A), which are comparatively low-melting, and (B), which are high-melting. The *methiodide* (A) is produced by the direct combination of the base with methyl iodide at 100°, and in contrast to the behaviour of methoxymethyldihydrobrucidine under similar conditions no oxidation accompanies this reaction (compare p. 1629). This methiodide yields the *methochloride* (A) by the action of silver chloride, and it was observed that both of these substances readily revert to the parent base. The methiodide loses methyl iodide quantitatively at 170°, whilst methyl chloride is eliminated when the methochloride is boiled with methyl-alcoholic potassium hydroxide. Methoxymethyltetrahydrobrucidine combines slowly with methyl sulphate when heated with an excess of the reagent in dry benzene for 24 hours, and yields a glassy mass which is a mixture of two *dimethosulphates*, namely, (A) and (B). These have not been separated, but the addition of sodium iodide to their aqueous solution precipitates the *dimethiodide* (B), m. p. 287°, the isomeride (A) remaining in solution. The dimethiodide (B) and the *dimethochloride* (B), which is prepared from it by means of silver chloride, each lose one molecule of methyl iodide, or methyl chloride, when heated, and yield respectively the *methiodide*, or *methochloride*, of the series (B). Attempts to prepare methyl-ψ-dihydrobrucidine by further decomposition of the dimethochloride (B) or the metho-

chloride (B) were unsuccessful, because decomposition of the rest of the molecule precedes the elimination of methyl chloride; this behaviour is in marked contrast to that of the corresponding strychnidine derivatives (compare this vol., p.1592). *Methoxymethyltetrahydrobrucidine dimethiodide* (A), m. p. 230—232°, is precipitated in a very crude condition by the addition of a large excess of potassium hydroxide to the mother-liquors from the preparation of the dimethiodide (B). It may also be obtained by the direct combination of the base with methyl iodide at 140°. When heated at its melting point, it loses one molecule of methyl iodide with the formation of the methiodide (B), and it is converted by silver chloride into the *dimethochloride* (A). When this substance is heated, two molecules of methyl chloride are liberated and methoxymethyltetrahydrobrucidine is regenerated. The relationships of these substances are illustrated by the following scheme :—



The ferric chloride reactions suggest that the metho-salts (A) and (B) are constituted analogously to the related series from methoxymethyldihydrobrucine.

The methiodide (A) will have the formula

$$(MeO)_2(C_{20}H_{22}O)(OMe)(:NMe)\left\langle \begin{matrix} CH_2 \\ NMe \end{matrix} \right\rangle I,$$

whilst the methiodide (B) should be

$$(MeO)_2(C_{20}H_{22}O)(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ N \end{matrix} \right\rangle I.$$

This is in agreement with the production of the methiodide (B) from each of the stereoisomeric dimethiodides (A) and (B), since the decomposition, on the suggested hypothesis, occurs at the nitrogen atom which becomes asymmetric (*Nabcd*) on the formation of the dimethiodides. A glance at the formula of the dimethiodides, $(MeO)_2(C_{20}H_{22}O)(OMe)(:NMe_2)\left\langle \begin{matrix} CH_2 \\ NMe \end{matrix} \right\rangle I_2$, will show that the $:NMe_2$ group is not a new asymmetric centre, whilst the nitrogen atom of the

$-CH_2-\overset{\diagup}{\underset{\diagdown}{N}}Me$ group can give rise to enantiomorphism. If the formulæ for the methiodides (A) and (B) were transposed, we should anticipate that the dimethiodides (A) and (B) would give rise to stereoisomeric methiodides on decomposition.

The *methyl*neo*dihydrobrucidinium salts* could not be prepared directly from methoxymethyltetrahydrobrucidine because this substance, unlike the methoxydihydro-base, is unaffected by boiling dilute sulphuric acid. Attempts to obtain these salts by the reduction of the methyl*neo*brucidinium salts were unsuccessful, as the sulphate was unchanged by electrolytic reduction. Methoxymethyltetrahydrobrucidine dihydrochloride, however, decomposes above its melting point in boiling mesitylene, yielding hydrogen chloride, methyl alcohol, and *methyl*neo*dihydrobrucidinium chloride*. This substance is amorphous, and its aqueous solution forms no precipitate with ammonia or potassium hydroxide. When the dry chloride is heated, it decomposes without producing methyl-ψ-dihydrobrucidine (compare this vol., p. 1592). The crystalline *methyl*neo*dihydrobrucidinium iodide* is prepared from the chloride by means of sodium iodide.

A number of efforts were made to prepare *methyl-ψ-dihydrobrucidine* by heating either (i) methoxymethyltetrahydrobrucidine methochloride (B), or (ii) methoxymethyltetrahydrobrucidine dimethochloride (B), or (iii) methyl*neo*dihydrobrucidinium chloride In each case, it was evident that decomposition of the rest of the molecule preceded the liberation of methyl chloride or of hydrogen chloride as the case might be, although the corresponding derivatives of strychnidine yield methyl-ψ-dihydrostrychnidine. We hoped, therefore, that the less stable *methoxymethyltetrahydrobrucidine dimethohydrogencarbonates* would decompose more readily, and this proved to be the case. The *dimethohydrogencarbonates* (A) and (B) may be prepared by evaporating in an open basin aqueous solutions of the corresponding *dimethohydroxides*, prepared by the action of silver hydroxide on the dimethiodides (A) and (B). They are also obtained by the action of silver carbonate on the dimethiodides. When heated over a flame, the dimethohydrogencarbonate (A) regenerates methoxymethyltetrahydrobrucidine, whilst the dimethohydrogencarbonate (B) yields methyl-ψ-dihydrobrucidine, $C_{24}H_{32}O_3N_2$, m. p. 220—221°, which has been characterised further by the preparation of a *dihydriodide*. When heated less vigorously (at 135°), the dimethohydrogencarbonate (B) loses only one molecule of carbon dioxide and forms *methoxymethyltetrahydrobrucidine methohydrogencarbonate* (B), which was not purified, but was isolated in the form of the methiodide (B) by the action of sodium iodide.

EXPERIMENTAL.

Brucine Methosulphate.—Leuchs and Anderson (*Ber.*, 1911, **44**, 3046) have described the preparation of small quantities of this substance by the combination of brucine with methyl sulphate in chloroform. The following process was found convenient for large-scale operations. Pure methyl sulphate (50 c.c.) is added to a suspension of brucine (125 g.) in methyl alcohol (200 c.c.). The base dissolves with evolution of heat, and the methosulphate, which separates over-night, is collected, washed with a little methyl alcohol, and dried first in a vacuum and then at 100°. A further quantity is obtained on concentrating the mother-liquors (total yield, about 90%). The methosulphate crystallises from ethyl alcohol in colourless needles, m. p. 278° (decomp.) (Found: C, 58·2; H, 6·5. Calc.: C, 58·5; H, 6·5%). Leuchs and Anderson give m. p. 268°.

Brucine methiodide is obtained by adding sodium iodide solution to an aqueous solution of the methosulphate. It crystallises from water in needles, m. p. 295° (decomp.), after drying at 100° (Found: C, 53·4; H, 5·4. Calc.: C, 53·7; H, 5·4%). Claus and Röhre (*Ber.*, 1881, **14**, 772) prepared this compound by the interaction of brucine and methyl iodide, and give the melting point as 290° (decomp)., whereas Hanssen (*Ber.*, 1884, **17**, 2267) gives 270°.

Brucine methohydrogencarbonate is prepared from the methiodide by shaking a hot aqueous solution with excess of silver carbonate, evaporating the filtrate to dryness under reduced pressure on the water-bath, and crystallising the residue from ethyl alcohol. It forms creamy-yellow plates, m. p. 202—203° (decomp.), which retain a molecule of alcohol after drying in a vacuum desiccator, and dissolve readily in water (loss at 120°, 10·5. 1EtOH requires loss, 9·8%. Found in dried material: C, 63·6; H, 6·5. $C_{23}H_{26}O_4N_2$, $MeHCO_3$ requires C, 63·8; H, 6·4%).

The Electrolytic Reduction of Brucine. Brucidine and Tetrahydrobrucine.

The success of this reduction depends largely on the temperature of the cathode chamber. Thus at 18°, the lowest temperature at which the battery of cells could be kept during a prolonged period in the absence of ice-cooling, about 68% of the weight of brucine used was isolated in the form of practically pure brucidine and tetrahydrobrucine. If, on the other hand, the temperature rose to 21°, the yield dropped to about 55% of the weight of brucine, and further the isolation of the tetrahydrobrucine was made more difficult by the presence of gummy substances, which caused the products to

become red when exposed to light and air. The formation of these could never be entirely avoided, but their amount was diminished considerably at the lower temperature. Tafel and Naumann (*loc. cit.*) were troubled by similar unstable by-products if their reduction was carried out above 15°.

The following is a description of a typical experiment, but it must be realised that variations occurred in the yields from different preparations. A solution of brucine (100 g.) in dilute sulphuric acid (300 g. of concentrated acid in 300 c.c. of water) is reduced in the usual apparatus (J., 1924, **125**, 1798) for 16 hours by a current of 5 amps., while the temperature is maintained at 17—18° by immersing the cells in running water. The contents of the cathode chambers and the aqueous washings of the cells are diluted to about twice the volume of the original solution, filtered in order to remove some lead sulphate, mixed with ice, and rendered alkaline by ammonia (*d* 0·880). Any rise of temperature is carefully avoided by the addition of ice and by cooling in a freezing mixture. A pale pink gum separates and adheres to the walls of the vessel. The liquid is decanted, extracted three times with chloroform (300 c.c. in all), and the mixed extracts are then used to dissolve the gum. The chloroform solution is washed with water, dried by potassium carbonate, and distilled. In order to remove the last traces of chloroform, the gummy residue is dissolved in boiling methyl alcohol (150 c.c.), and the solution evaporated to dryness on the water-bath. The product (100 g.), now a solid, is dissolved in boiling methyl alcohol (250 c.c.), and, on cooling, an almost colourless mass of crystals separates; this is collected and dried on the water-bath (45 g.). It melts at about 199° and is practically pure brucidine (see below). The mother-liquors are evaporated to dryness on the water-bath, the last traces of solvent being removed under reduced pressure; on boiling the semi-solid mass with pure ethyl acetate, a part remains undissolved, and after cooling is collected, washed with ethyl acetate, and dried in a vacuum (23 g.). It melts at 174° and is practically pure tetrahydrobrucine (see below). The mother-liquors contain the oily by-products, together with some crystalline substances, and their investigation is in progress.

Brucidine.—The product obtained from the reduction is crystallised from methyl alcohol, from which it separates in colourless needles, which, after being dried in a vacuum desiccator, shrink at 188—190° and melt at 203—203·5° without decomposition. On drying at 105° brucidine loses one molecule of methyl alcohol of crystallisation, and then melts at 203—203·5° without decomposition (loss at 105°, 7·7. 1MeOH requires loss, 7·9%. Found in dried material: C, 72·7; H, 7·3. $C_{23}H_{28}O_3N_2$ requires C, 72·6; H, 7·4%). It is

very slightly soluble in boiling water, and the solution reacts alkaline to litmus. It dissolves readily in chloroform, less easily in methyl alcohol and ethyl acetate, and only very sparingly in ether. The colourless solution of a pure specimen in dilute hydrochloric acid slowly acquires a faint olive-green colour; on addition of a few drops of sodium nitrite a dark green coloration appears, which becomes reddish-brown on standing. When now excess of sodium carbonate is added, the colour changes to a very intense claret, which passes entirely into chloroform when the liquid is shaken with that solvent. These properties agree well with the reactions of the substance which Tafel and Naumann describe as "tetrahydrobrucine." A solution of brucidine in 60% sulphuric acid * to which a drop of an aqueous solution of potassium dichromate has been added becomes green on standing. The addition of ferric chloride to a solution in dilute hydrochloric acid produces a dark blue-green colour, which appears pink when examined in thin layers. These colour reactions are also shown by many derivatives of brucidine (see p. 1661) and in many cases dilute nitric acid causes the development of a similar green-pink colour.

The corresponding colour reactions of brucine may be given here for comparison. A drop of dichromate imparts a deep red colour to a solution in 60% sulphuric acid, but the addition of ferric chloride to brucine in dilute hydrochloric acid does not produce a coloration.

The *dihydrochloride* is formed when a little concentrated hydrochloric acid is added to a solution of the base in hot methyl alcohol. On cooling, the liquid sets to a mass of needles, which are collected and recrystallised from methyl alcohol. This salt forms colourless needles which begin to darken at 285°, and melt at 310° (decomp.) after drying in a vacuum desiccator. A satisfactory analysis of this substance was not obtained, as it appears to lose hydrogen chloride on drying. There is no doubt, however, that the base combines with two molecules of hydrogen chloride. A solution of the dihydrochloride in methyl alcohol is colourless, but on exposure for a short time to air it becomes green; the solution then appears pink when examined in thin layers.

The *dihydriodide*, prepared by adding sodium iodide to a solution of the base in dilute hydrochloric acid, crystallises from water in shining, grey needles, m.p. 255° (decomp.), which are only very sparingly soluble in hot water.

The methosulphate. A short, vigorous reaction occurs when pure methyl sulphate (8 c.c.) is added to a slightly warm suspension of

* In the case of brucine and its derivatives the colour reactions are well shown in dilute sulphuric acid of 60% by weight, and not by volume (compare Part IV, this vol., p. 1599).

powdered brucidine (20 g.) in methyl alcohol (80 c.c.), and when this has subsided the mixture is heated on the water-bath for a few moments until the base has completely dissolved. On cooling the green solution in ice, the methosulphate separates in excellent yield as a mass of colourless needles, which are collected, washed with methyl alcohol, and dried in a vacuum desiccator. It is essential that the methyl sulphate should be pure and freshly distilled; the presence of acid greatly reduces the yield. When prepared in this way, the methosulphate is sufficiently pure for most purposes. It may be recrystallised from methyl alcohol in colourless needles which begin to darken at 270° and melt at 291° (decomp.), are readily soluble in water, and become purple or green when kept for some time.

The *methiodide* is obtained either by the addition of sodium iodide to an aqueous solution of the methosulphate, or by adding methyl iodide to an ethyl-alcoholic solution of the base. In either case, the crystals which separate are recrystallised from water. The methiodide forms colourless needles, m. p. 322° (decomp.), which are sparingly soluble in methyl or ethyl alcohol (Found: C, 55·1; H, 6·0. $C_{23}H_{28}O_3N_2$,MeI requires C, 55·2; H, 5·9%).

Tetrahydrobrucine.—The product obtained from the electrolytic reduction (p. 1636) is recrystallised from ethyl acetate, in which it is sparingly soluble. When prepared in this way, tetrahydrobrucine forms colourless needles, m. p. 177° (Found: C, 69·1; H, 7·7. $C_{23}H_{30}O_4N_2$ requires C, 69·4; H, 7·5%), but one of its characteristic properties is the power of retaining solvent of crystallisation with the resulting production of comparatively low-melting crystalline forms. It melts in boiling water, dissolves fairly readily to a solution which is alkaline to litmus, and on cooling crystallises in colourless needles; after drying for a short time in a vacuum desiccator, these melt to a pasty mass at 90—92°, and evolve water briskly at 100° (loss at 100°, 14·8. $4H_2O$ requires loss, 15·3%). It is rather easily soluble in methyl alcohol, but when a concentrated solution is cooled, it crystallises in colourless needles, which, after being dried in a vacuum desiccator, melt to a pasty mass at 90—95° (loss at 100°, 10·4. MeOH requires loss, 10·8%), harden on further heating, and melt again at 177°. When crystallised from ethyl alcohol, tetrahydrobrucine forms colourless needles, which soften at 115° and melt at 120° after drying in a vacuum desiccator. These contain one molecule of ethyl alcohol which is not lost at 90° (Found in material dried at 90°: C, 68·4; H, 8·3. $C_{23}H_{30}O_4N_2$,EtOH requires C, 68·2; H, 8·2%), but is liberated at 120° (loss at 120°, 10·0. 1EtOH requires loss, 10·4%). A solution of a pure specimen in dilute hydrochloric acid is colourless, but becomes bright green

on the addition of a few drops of ferric chloride; this solution does not, however, show the pink tinge in thin layers which is characteristic of brucidine and its derivatives.

The *dihydrochloride* is rather readily soluble, but is obtained when a little concentrated hydrochloric acid is added to a concentrated solution of the base in methyl alcohol. On standing over-night, it separates in colourless needles, which are collected, washed with methyl alcohol, and dried at 100°. This salt darkens at 280° and melts at 305° (decomp.) (Found: C, 58·4; H, 7·0. $C_{23}H_{30}O_4N_2,2HCl$ requires C, 58·6; H, 6·8%).

The *dihydriodide* is prepared by adding sodium iodide to a solution of tetrahydrobrucine in dilute hydrochloric acid. The green colour of the solution disappears, and a yellow gum separates which slowly crystallises on rubbing. When recrystallised from ethyl alcohol, it forms colourless plates, which darken at 220° and melt at 225° (decomp.).

The *methiodide* is readily obtained by warming a solution of the base and an excess of methyl iodide in methyl alcohol for a few moments until crystallisation begins. After cooling, the colourless needles of the methiodide are collected, washed, and dried in a vacuum desiccator; they then melt at 290° (decomp.) (loss at 100°, 5·3. 1MeOH requires loss, 5·5%. Found in material dried at 100°: C, 53·5; H, 6·3. $C_{23}H_{30}O_4N_2,MeI$ requires C, 53·3; H, 6·1%).

The nitrosoamine. Sodium nitrite (0·5 g.) in a little water is added gradually to a cooled solution of tetrahydrobrucine (2 g.) in hydrochloric acid (20 c.c. of 2*N*). The yellow crystals are collected, washed with dilute hydrochloric acid, and recrystallised from ethyl alcohol. *Tetrahydrobrucine nitrosoamine hydrochloride* forms buff-coloured needles, which, after drying in a desiccator, darken and shrink at 190°, have become black at 250°, and melt at 288° (decomp.) (loss at 100°, 8·5. 1EtOH requires loss, 9·0%. Found in material dried at 100°: Cl, 7·5. $C_{23}H_{29}O_5N_3,HCl$ requires Cl, 7·6%).

When sodium carbonate is added to an aqueous solution of the hydrochloride, the *nitrosoamine* separates in needles. It is collected, washed, and recrystallised from dilute ethyl alcohol, separating in lemon-yellow needles which shrink at 205° and melt at 213—214° (decomp.) (Found: C, 64·2; H, 6·7. $C_{23}H_{29}O_5N_3$ requires C, 64·6; H, 6·8%). It is readily soluble in ethyl alcohol, and gives Liebermann's nitroso-reaction.

The Conversion of Tetrahydrobrucine into Brucidine.

A mixture of tetrahydrobrucine (5 g.) and phosphorus oxychloride (50 g.) is warmed on the water-bath for about 30 minutes; hydrogen chloride is evolved, whilst the base becomes gummy, partly dissolves,

and soon changes to a mass of crystals. The excess of phosphorus oxychloride is removed by distillation on the water-bath under reduced pressure, and the residue is dissolved in water (25 c.c.), much heat being produced. After cooling and addition of ice, the solution is mixed with potassium hydroxide, and the semi-solid precipitate is collected on a glass rod, drained as thoroughly as possible, and boiled with a little methyl alcohol. The product becomes crystalline, and after cooling it is collected, washed with methyl alcohol, and dried at 100° (yield 3·6 g.; 75% of that theoretically possible). The crystals melt at 203—203·5° either alone or when mixed with a specimen of brucidine.

The Electrolytic Reduction of Methylbrucine. Brucidine Metho-hydroxide and Metho-salts.

Methylbrucine.—The conversion of brucine methosulphate into methylbrucine does not take place under conditions similar to those under which strychnine methosulphate yields methylstrychnine (this vol., p. 1624), because the methosulphate is precipitated unchanged by the alkali. If, however, a higher temperature and more concentrated potassium hydroxide are used, the liquid sets to a gelatinous mass, which certainly contains methylbrucine, but which can be neither crystallised nor purified. Methylbrucine was therefore prepared by a modification of the method of Leuchs and Anderson (*loc. cit.*, p. 3047), who used less concentrated alkali. Hot, dilute sodium hydroxide solution (200 c.c. of 2·5*N*) is added in one batch to a hot solution of brucine methosulphate (10 g.) in water (50 c.c.), and the mixture is heated on the water-bath for 5 minutes. On cooling, the yellow solution does not gelatinise (compare Leuchs and Anderson); sodium hydroxide (20 c.c. of 30%) is now added, and the mixture set aside. Next day, the needles, which fill the liquid, are collected, and are sufficiently pure for the purpose of the reduction described below. When purified by the addition of acetone to a concentrated aqueous solution, and dried at 100°, methylbrucine forms colourless needles, m. p. 300° (decomp.) when heated quickly. Leuchs and Anderson give the melting point as 300° (decomp.).

The reduction. A solution of methylbrucine (20 g.) in sulphuric acid (100 c.c. of 60%) is reduced in the usual apparatus for 6 hours with a current of 5 amps., while the temperature is kept at 18° by cooling in running water. The liquid is diluted with an equal volume of water, heated on the water-bath, and neutralised by an excess of barium carbonate. The deep red filtrate, mixed with the washings of the barium precipitate, is evaporated to dryness under reduced pressure on the water-bath. The dark red, glassy residue

dissolves readily in water or methyl or ethyl alcohol, and shows very little tendency to crystallise. A small specimen, however, was obtained in a crystalline condition from methyl alcohol by cooling in ice. It was recrystallised once from that solvent in colourless nodules of needles, m. p. 265° (decomp.) after drying in a vacuum desiccator, and appears from analysis to be *brucidine methohydrogencarbonate* containing two molecules of water (Found: C, 60·3; H, 7·1. $C_{25}H_{32}O_6N_2,2H_2O$ requires C, 61·0; H, 7·3%). This view is confirmed by the conversion of this substance into brucidine methiodide and methohydroxide (see below), and also by its interaction with dilute hydrochloric acid. Carbon dioxide is evolved, and the substance dissolves to a green solution; the addition of ferric chloride intensifies this colour, and gives it the pink tinge in thin layers which is characteristic of brucidine and its derivatives.

When sodium iodide is added to an aqueous solution of the methohydrogencarbonate, brucidine methiodide is formed. It separates from water in colourless needles, m. p. 322° (decomp.), and is identical with a specimen prepared from brucidine (p. 1638).

Brucidine methohydroxide is obtained by grinding the crude methohydrogencarbonate with 30% potassium hydroxide solution. The resulting crystalline paste is filtered, and the solid recrystallised twice from water, in which it dissolves very readily. Brucidine methohydroxide forms colourless, hair-fine needles, m. p. 268° (decomp.), which retain two molecules of water after drying in a vacuum desiccator (Found: C, 64·1; H, 7·6. $C_{23}H_{28}O_3N_2,MeOH,2H_2O$ requires C, 64·3; H, 8·0%). The same substance was prepared for comparison from brucidine methiodide. An aqueous solution of the methiodide was shaken with an excess of silver carbonate, and the dark red filtrate evaporated to dryness under reduced pressure on the water-bath. The residual dark red glass (not purified) was dissolved in water, and mixed with 50% potassium hydroxide solution; brucidine methohydroxide then separated in crystalline form, and was recrystallised from a little water in colourless needles, m. p. 268° (decomp.).

The specimen obtained from the reduction of methylbrucine was converted into brucidine methiodide either (i) by adding sodium iodide to a solution in dilute hydrochloric acid, or (ii) when a solution of the methohydroxide (4 g.) and methyl iodide (10 c.c.) in ethyl alcohol (30 c.c.) was boiled for 10 minutes, and then cooled. In either case, the crystalline precipitate which separated was recrystallised from water, and formed colourless needles, m. p. 322° (decomp.) (Found: C, 55·1; H, 6·1. $C_{23}H_{28}O_3N_2,MeI$ requires C, 55·2; H, 5·9%). The identity of this substance with brucidine methiodide was confirmed by converting it into methoxymethyldihydrobrucidine

(see below), which is formed by heating brucidine metho-salts with methyl-alcoholic potassium hydroxide. Brucidine methochloride (not purified), prepared by shaking with an excess of silver chloride an aqueous solution of the methiodide obtained above, and evaporating the filtrate to dryness under reduced pressure on the water-bath, was heated with a large excess of 25% methyl-alcoholic potassium hydroxide for 30 minutes, cooled, mixed with water, and the precipitate collected. Crystallisation from ethyl alcohol yielded colourless needles, m. p. 115° either alone or mixed with an authentic specimen of methoxymethyldihydrobrucidine.

Methoxymethyldihydrobrucidine.—A mixture of brucidine methosulphate (30 g.) and methyl-alcoholic potassium hydroxide (150 c.c. of 25%) is heated on the water-bath for 30 minutes in an open flask so that the methyl alcohol partly evaporates. The initial yellow solution gradually clouds and deposits a solid precipitate which increases on cooling in running water. Water (500 c.c.) is added, and the precipitate is collected after 1 hour, washed with water, and dried roughly on porous tile. The crude product is crystallised from ethyl alcohol, from which about 20 g. of pure material separate, and the addition of water to the mother-liquor yields a further quantity of practically pure substance (total yield, *ca.* 90%). *Methoxymethyldihydrobrucidine* forms colourless needles, m. p. 115° without decomp. after drying in a vacuum [Found: C, 70·2; H, 7·8; OMe, 21·9. $C_{25}H_{34}O_4N_2$ requires C, 70·4; H, 8·0; $(OMe)_3$, 21·8%]. It distils without decomposition at 265—267°/1·5 mm., and is rather readily soluble in the usual solvents except light petroleum. A solution in glacial acetic acid is not precipitated on addition of water. The base and its solutions become red on keeping, especially if exposed to laboratory fumes.

The dihydriodide. The addition of sodium iodide to a solution of methoxymethyldihydrobrucidine in dilute sulphuric acid produces a red, uncrystallisable oil, which rapidly oxidises, but when concentrated sodium iodide solution is added slowly with constant stirring to a solution of the base (5 g.) in 2*N*-sulphuric acid (20 c.c.), saturated with sulphur dioxide, an additive compound separates as a brick-red oil which soon crystallises on rubbing. This is collected (approximately 8 g.), and boiled with water until the orange colour of the solution and the smell of sulphur dioxide have disappeared; the dihydriodide then crystallises on cooling in colourless leaflets, m. p. 217—218° (decomp.) (loss at 100°, 3·5. $1\frac{1}{2}H_2O$ require loss, 3·8%. Found in material dried at 100°: C, 43·8; H, 5·3. $C_{25}H_{34}O_4N_2,2HI$ requires C, 44·0; H, 5·3%). The crystals become yellow on keeping, on exposure, or on drying, and when heated char and evolve hydrogen iodide.

The methiodide (*A*). This substance is obtained under the following conditions. (i) Methoxymethyldihydrobrucidine (10 g.) and pure methyl iodide (15 c.c.) are heated together at 100° in a sealed tube for 5 minutes. The solution becomes purple and fills with crystals, which are collected after cooling, washed with methyl iodide, and dried in a vacuum (12 g.). The mother-liquors deposit a further amount (1 g.) on standing over-night. The yield is about 98%. (ii) A mixture of methoxymethyldihydrobrucidine (15 g.) and methyl iodide (15 c.c.) is boiled under reflux for 15 minutes, and next day 13—15 g. of crude product are collected. The methiodide obtained by either method separates from methyl alcohol in creamy tablets which become chalky when dried in a vacuum; m. p. 190° (loss at 100°, 2·6. 0·5MeOH requires loss, 2·8%. Found in material dried at 100°: C, 55·1; H, 6·5; N, 4·9. $C_{25}H_{34}O_4N_2$,MeI requires C, 55·0; H, 6·5; N, 4·9%). It crystallises from water in stout prisms, m. p. 190°, or from ethyl alcohol in rectangular plates, m. p. 179°, which contain alcohol of crystallisation (loss at 100°, 3·6. 0·5EtOH requires loss, 3·9%. Found in dried material: C, 55·2; H, 6·7%). It yields the methochloride (A) when treated with silver chloride (see below).

The methyl-alcoholic mother-liquors gradually deposit a very small amount of crystalline material which does not contain iodine. This is recrystallised by dissolving it in much methyl alcohol and concentrating the solution; *oxymethoxymethyldihydrobrucidine* then separates in pink bipyramids, which shrink at 270° and melt at 277° (decomp.) (Found: C, 67·3; H, 7·6. $C_{25}H_{34}O_5N_2$ requires C, 67·9; H, 7·7%). The same substance may be obtained in greater quantity by a simpler method. When a solution of methoxymethyldihydrobrucidine in ethyl alcohol containing a few crystals of iodine is exposed to the air for some days, the solution becomes deep crimson, and gradually deposits oxymethoxymethyldihydrobrucidine as pale pink, perfectly formed prisms, which soften at 270°, melt at 277°, and are analytically pure (Found: C, 67·6; H, 7·8; N, 6·1. $C_{25}H_{34}O_5N_2$ requires N, 6·3%). It is very sparingly soluble in ethyl alcohol or acetone, but dissolves in warm benzene, and is readily soluble in chloroform. It is insoluble in boiling water or sodium hydroxide, but dissolves readily in dilute hydrochloric acid. When it is boiled with methyl alcohol (charcoal) and the filtered solution is concentrated, a slightly more soluble base separates in irregular, boat-shaped crystals, m. p. 270° (decomp.), which appear from the analysis to be *dioxymethoxymethyldihydrobrucidine* (X) (compare pp. 1647, 1648) (Found: C, 65·5; H, 7·4. $C_{25}H_{34}O_6N_2$ requires C, 65·5; H, 7·4%).

When methoxymethyldihydrobrucidine and methyl iodide inter-

act in methyl-alcoholic solution the reaction follows a course very similar to that, described above, in the absence of methyl alcohol, and the chief product is the monomethiodide (A), accompanied by small quantities of oxymethoxymethyldihydrobrucidine (compare Part IV, this vol., p. 1607). In addition to these substances, an intermediate *base*, m. p. about 210—218°, appears to be formed. This does not contain iodine, and changes into oxymethoxymethyldihydrobrucidine in boiling methyl alcohol or acetone, in which solvents it is sparingly soluble. This substance was not obtained sufficiently pure for analysis, and the change evidently takes place so readily that the intermediate product did not appear in some experiments, but had been completely converted into oxymethoxymethyldihydrobrucidine. The following is an account of an experiment in which the intermediate base was formed. A mixture of methoxymethyldihydrobrucidine (5 g.) and methyl iodide (5 c.c.) in methyl alcohol (25 c.c.) was boiled under reflux for 3 hours, and then concentrated to half its volume. The residue was cooled for several hours in ice and salt, and the crystals which had separated were collected, washed with methyl alcohol, and dried (3 g.). The mother-liquors were examined separately (see below). The crude crystals were extracted with boiling methyl alcohol (20 c.c.), and the insoluble portion was collected, washed thoroughly with methyl alcohol, and dried (0·2 g.). It consisted of indefinite crystals, m. p. 210°, which did not contain iodine. The methyl-alcoholic extract contained practically pure methiodide (A).

The methyl-alcoholic mother-liquors (see above) were mixed with water, and the solid was collected and extracted with boiling methyl alcohol. The insoluble portion (0·1 g.) formed indefinite crystals, m. p. 218°, which did not contain iodine. Oxymethoxymethyldihydrobrucidine separated in the characteristic bipyramids, m. p. 277°, when a solution of the mixed fractions, m. p. 210° and 218°, in much boiling methyl alcohol was concentrated and cooled.

The Action of Methyl-alcoholic Potassium Hydroxide on the Methiodide (*A*) *and the Methochloride* (*A*).—The reaction follows the same course in both cases, but takes place more readily with the methochloride. This is prepared from the methiodide by heating an aqueous solution with excess of silver chloride for 1 hour, and evaporating the filtrate to dryness on the water-bath under reduced pressure. The gummy *methochloride* crystallises in colourless needles on standing for some days. The methochloride (7 g.) and methyl-alcoholic potassium hydroxide (60 c.c. of 25%) are heated in an open flask on the water-bath for 40 minutes, and after cooling and addition of water, the precipitate is collected and dried in a desiccator (5 g.). Recrystallisation of this crude material from ethyl alcohol

yields colourless needles; m. p. 115°, either alone or mixed with a specimen of methoxymethyldihydrobrucidine (Found: C, 70·6; H, 7·8; OMe, 21·4%). A careful examination of the mother-liquors yields no other product.

Methoxymethyldihydrobrucidine methochloride (*B*) cannot be obtained directly from methoxymethyldihydrobrucidine, but it is formed when methoxymethyldihydrobrucidine dimethochloride (B) (compare p. 1647) (15 g.) is heated in boiling nitrobenzene (30 c.c.) until all has dissolved and the evolution of gas appears to have ceased—10 to 15 minutes. After standing over-night, the crystals which have separated are collected, washed with light petroleum, dried in a desiccator (10 g.), and crystallised from acetone, being thus obtained in colourless prisms, m. p. 164° (decomp.) (Found: C, 64·9; H, 7·4. $C_{25}H_{34}O_4N_2$,MeCl requires C, 65·5; H, 7·8%). This substance yields methyl-ψ-brucidine when heated gently in a test-tube over a free flame (compare p. 1651). The nitrobenzene mother-liquors contain both methyl-ψ-brucidine and methyl-ψ-brucidine methochloride; their examination is described on p. 1652.

The *methiodide* (*B*) is prepared from the methochloride with sodium iodide, but has not been obtained in any other way. It crystallises from water in colourless, coarse prisms, m. p. 291° (decomp.), and is less soluble in water and methyl or ethyl alcohol than the isomeric methiodide (A).

The *dimethiodide* (*A*) is obtained when methoxymethyldihydrobrucidine (5 g.) and pure methyl iodide (10 c.c.) are heated in a sealed tube in an oil bath at 135—140° for 7½ hours. After removal of the methyl iodide by distillation, the brown, sandy powder (8·5 g.) is crystallised from methyl alcohol (charcoal), from which the dimethiodide (4·5 g.) separates in pink leaflets which become colourless at 110°, form a pasty mass at 215°, and evolve gas freely at 230° (loss at 110°, 8·6. 2MeOH requires loss, 8·3%. Found in material dried at 110°: C, 45·3; H, 5·5. $C_{25}H_{34}O_4N_2$,2MeI requires C, 45·6; H, 5·6%).

The *methosulphate* (*A*) is formed when a solution of methoxymethyldihydrobrucidine (3 g.) and pure methyl sulphate (10 c.c.) in dry benzene (70 c.c.) is boiled under reflux for 4 hours and allowed to remain over-night. A mixture of stellar aggregates of coarse crystals and a purple gum separates, and the crystals of the monomethosulphate are easily detached and pressed on porous tile (1·7 g.). The gum consists essentially of the dimethosulphate (B) (see below). The methosulphate is crystallised from ethyl alcohol, in which it is rather readily soluble, and forms colourless, rectangular plates, m. p. 231—232° (decomp.) (Found: S, 6·0. $C_{25}H_{34}O_4N_2$,Me_2SO_4 requires S, 5·8%). This substance is

very soluble in water and is converted by sodium iodide into the methiodide (A), m. p. 190°.

The Dimethosulphate (*B*) *and the Dimethiodide* (*B*).—A solution of carefully dried methoxymethyldihydrobrucidine (60 g.) and pure methyl sulphate (150 c.c.) in dry benzene (500 c.c.) is boiled for 9 hours under reflux, carefully protected from moisture. It rapidly becomes purple, and after some time a brown gum forms slowly and increases steadily with diminution of the purple colour. After the benzene has been decanted, the gum is washed with benzene, and freed from excess of the solvent by a current of air. It undoubtedly consists essentially of the *dimethosulphate* (*B*), although traces of benzene and methyl sulphate are still present, but all attempts to crystallise it are unsuccessful, and it is therefore converted into the corresponding dimethiodide by sodium iodide. Sodium iodide (100 g.) in warm water (40 c.c.) is added to the dimethosulphate in warm water (100 c.c.) and, after cooling, the mixture is scratched and set aside over-night. The crystalline precipitate is collected, washed with water, dried in a vacuum desiccator (84 g.), and recrystallised from water. The *dimethiodide* (*B*) forms colourless columns, m. p. 290° (decomp.), with darkening below this, and is sparingly soluble in alcohol (loss at 105°, 1·0. $\frac{1}{2}H_2O$ requires loss, 1·2%. Found in dried material: C, 45·0; H, 5·5. $C_{25}H_{34}O_4N_2.2MeI$ requires C, 45·6; H, 5·6%).

The mother-liquors from the precipitation with sodium iodide are mixed with 50% potassium hydroxide solution; the caseous precipitate then soon hardens. It is washed roughly with water, and boiled with alcohol, which causes it to crystallise without passing into solution. After cooling, the crystals are collected (13 g.), and recrystallised from water, being obtained in colourless columns, m. p. 290° (decomp.), identical with those obtained by direct precipitation from the solution of the dimethosulphate with sodium iodide (loss at 105°, 1·1%. Found in dried material: C, 45·5; H, 5·4%). The total yield is 97 g., or 96% of that theoretically possible.

The dimethiodide is stable to 25% methyl-alcoholic potassium hydroxide at 120°, but reaction takes place with the corresponding dimethohydrogensulphate obtained by means of silver sulphate. The dimethiodide (10 g.) in water (75 c.c.) is heated on the water-bath for 1 hour with excess of silver sulphate, the filtrate is evaporated to dryness under reduced pressure on the water-bath, the residue taken up in methyl alcohol to eliminate silver sulphate, and the solution again evaporated to dryness. The gummy dimethohydrogensulphate thus obtained (not isolated) is mixed with methyl-alcoholic potassium hydroxide (100 c.c. of 25%) and heated in an

oil-bath for 45 minutes while the temperature is gradually raised from 110° to 130°. After cooling and addition of water, the roughly dried, sandy powder is crystallised from ethyl alcohol, and shown to be identical with methoxymethyldihydrobrucidine by mixed m. p., and by conversion into the methiodide (A), m. p. 190°.

The *dimethochloride* (*B*), prepared in the usual way from the dimethiodide by silver chloride, is a colourless glass which could not be crystallised.

Nitromethoxymethyldihydrobrucidine.—A solution of methoxymethyldihydrobrucidine (3 g.) in water (75 c.c.) and nitric acid (*d* 1·4; 7·5 c.c.) is heated under reflux on the water-bath for 2 hours. From the cooled mixture, ammonia (*d* 0·880) precipitates a negligible quantity of a base, which is discarded, and the addition of 50% potassium hydroxide solution yields a mixture of tar and crystals which is pressed on porous tile, crystallised twice from ethyl alcohol, and dried in a desiccator. *Nitromethoxymethyldihydrobrucidine* forms colourless needles, m. p. 276—278° (decomp.), which contain alcohol of crystallisation (loss at 110°, 9·6. 1EtOH requires loss, 9·8%. Found in material dried at 110°: C, 63·9; H, 7·0; N, 9·2. $C_{25}H_{33}O_6N_3$ requires C, 63·7; H, 7·1; N, 8·9%). It is rather curious that this substance exhibits the brucidine reaction with 60% sulphuric acid and potassium dichromate.

Permanganate Oxidation of Methoxymethyldihydrobrucidine. The Isomeric Dioxymethoxymethyldihydrobrucidines (*Y*) and (*Z*).

A number of experiments showed the necessity of adhering to the conditions described below. Powdered (80-mesh) potassium permanganate (20 g.; 4 atoms of oxygen) is added gradually to a solution of methoxymethyldihydrobrucidine (20 g.) in purified acetone (800 c.c.), stirred mechanically, and cooled in ice and salt so that the internal temperature remains at −10°. The manganese precipitate, collected and washed with acetone, yields with water a solution in which only oxalic acid can be detected.

The removal of the acetone by distillation yields 12—15 g. of thick, brown oil. When this is dissolved in warm alcohol (15 c.c.), cooled, and scratched, 2·5—2·8 g. of fairly pure crystalline material separate. (The examination of the mother-liquors, called M, is described on p. 1648.) Recrystallisation from ethyl alcohol yields colourless prisms, m. p. 185—186°, which appear from the analyses to be *dioxymethoxymethyldihydrobrucidine* (called Y; compare p. 1643) (loss at 100°, 4·4. ½EtOH requires loss, 4·8%. Found in dried material: C, 65·3; H, 7·6; N, 6·3. $C_{25}H_{34}O_6N_2$ requires C, 65·5; H, 7·4; N, 6·1%). This substance is insoluble in water or alkali, but readily dissolves in dilute hydrochloric acid, giving a green solution;

on addition of ammonia, the base is precipitated and the colour changes to red. The compound is recovered unchanged after boiling for a few minutes with acetic anhydride, and attempts to form a semicarbazone resulted in a dark red, uncrystallisable oil.

The *methiodide* is prepared by heating the base (2 g.) and methyl iodide (3 c.c.) in a sealed tube at 100° for 5 hours. The residue is pressed on porous tile, and separates from ethyl alcohol as a mixture of plates and needles, m. p. 223°. On recrystallisation from ethyl alcohol, both forms separate again, but when the mixture is boiled with insufficient alcohol for complete solution, the needles dissolve more rapidly, and ultimately the undissolved portion consists of plates only. These are collected and recrystallised, by seeding, from ethyl alcohol, separating in colourless plates, m. p. 225—226°, which lose nothing at 110° (Found: C, 52·3; H, 6·4. $C_{25}H_{34}O_6N_2$,MeI requires C, 52·0; H, 6·2%). When the hot alcoholic solution from the separation of plates and needles is cooled and set aside, it begins to deposit needles only, and on scratching, the material separates entirely in that form; but if allowed to remain undisturbed, the mixture of crystals again separates. The needles are recrystallised in the same form, m. p. 223—224°, from ethyl alcohol, and contain 2 molecules of alcohol of crystallisation after drying in a vacuum desiccator (loss at 110°, 12·1. 2EtOH requires loss, 13·3%. Found in material dried at 110°: C, 52·2; H, 6·4%). Both forms are sparingly soluble in ethyl alcohol, and a hot solution of each in that solvent, when cooled and seeded with the other form, deposits only that by which it has been seeded. A mixture of the two pure forms melts at 223°.

The alcoholic mother-liquors (M; p. 1647) are evaporated to dryness, and a filtered, aqueous solution of the residue is made strongly alkaline with potassium hydroxide. The oil thus precipitated is extracted as far as possible with ether, and the extract dried with potassium carbonate. The oil which remains undissolved in the ether yields no crystalline product, and is discarded. The oily residue from the evaporation of the ether is dissolved in ethyl alcohol (5 c.c.), cooled in ice and salt, and scratched frequently; crystals (3·2 g.) then separate slowly. Three recrystallisations from ethyl alcohol yield colourless, square plates, m. p. 110—111° after drying in a vacuum desiccator, which appear from analysis to be a *dioxymethoxymethyldihydrobrucidine* (called Z) (loss at 100°, 4·0. ½EtOH requires loss, 4·8%. Found in material dried at 100°: C, 65·0, 65·1; H, 7·6, 7·5; N, 5·8. $C_{25}H_{34}O_6N_2$ requires C, 65·5; H, 7·4; N, 6·1%). This substance is sparingly soluble in cold water, dissolves readily on heating to give a neutral solution, and on cooling separates in colourless, rectangular prisms. It is readily soluble in

the usual organic solvents except light petroleum, from which it crystallises when a hot solution is cooled, and gives the same colour reactions as methoxymethyldihydrobrucidine. It dissolves rapidly in cold dilute hydrochloric acid, but no iodide separates with sodium iodide. The compound is recovered unchanged after heating with excess of methyl iodide in a sealed tube at 100° for 4 hours, and an alcoholic solution does not form a sparingly soluble picrate.

Ethoxymethyldihydrobrucidine.—This substance was prepared in order to ascertain whether alkyloxy-groups other than methoxyl can be introduced into brucidine. The action between brucidine methosulphate and sodium ethoxide follows a similar course to that described on p. 1642 with methyl-alcoholic potassium hydroxide, but the isolation of the product was not successful, and further investigation was abandoned. Brucidine methosulphate (15 g.) and a solution of sodium (10 g.) in ethyl alcohol (150 c.c.) were heated in an open flask for 1 hour on the water-bath and then for 1 hour in an oil-bath at 120°. After cooling and addition of water, the sticky precipitate was pressed on porous tile. Attempts to crystallise the sandy powder (10 g.) thus obtained were fruitless, although it probably consisted of ethoxymethyldihydrobrucidine, and it was converted into the methiodide by boiling with excess of methyl iodide in ethyl alcohol (15 c.c.) for 20 minutes. On cooling, the purple solution set to a mass of crystals, which were washed with alcohol until they became colourless. *Ethoxymethyldihydrobrucidine methiodide*, recrystallised from ethyl alcohol, forms colourless needles, m. p. 176° (decomp.) (Found: C, 55·6; H, 7·1. $C_{26}H_{36}O_4N_2$,MeI requires C, 55·6; H, 6·9%).

*Methyl*neo*brucidinium Salts.*

*Methyl*neo*brucidinium Iodide.*—When a solution of methoxymethyldihydrobrucidine (25 g.) in sulphuric acid (250 c.c. of 10% by weight) is boiled gently under reflux for 2½ hours it becomes red, and methyl alcohol is evolved and can be burnt at the neck of the flask. The solution is cooled, rendered alkaline with ammonia (no precipitate), and just acidified with sulphur dioxide. The careful addition of concentrated sodium iodide precipitates a crystalline *iodide* (22 g.), which separates from water in stout, pink columns, m. p. 298° (decomp.) (Found: C, 55·3; H, 6·0. $C_{24}H_{31}O_3N_2I$ requires C, 55·2; H, 5·9%). When prepared in this way, the salt is always red; it may, however, be obtained practically colourless by crystallisation from aqueous potassium carbonate, or from ethyl alcohol, from which it separates in leaflets, m. p. 298° (decomp.). It is sparingly soluble in cold water, acetone, or methyl or ethyl

alcohol, and crystallises unchanged when a boiling solution in 30% potassium hydroxide is cooled.

The mother-liquors from the precipitation by sodium iodide (see above) were investigated in the expectation of isolating an isomeric iodide (compare methyl*neo*strychnidinium iodide, this vol., p. 1612), but only a further quantity of the same methyl*neo*brucidinium iodide was obtained, the total yield being 90% of that theoretically possible. The mother-liquors are concentrated to quite a small volume under reduced pressure on the water-bath, and after cooling, the aqueous layer is decanted from the oil which has separated during the distillation. This oil crystallises on being boiled with a little acetone; part dissolves, crystallisation begins suddenly, and the oil soon changes into a mass of colourless needles. After cooling, these are collected, washed with acetone, and dried (5 g.); m. p. 295° (decomp.). One recrystallisation from water yields the iodide in colourless, prismatic columns, m. p. 298° (decomp.). The identity of this substance with the methyl*neo*brucidinium iodide obtained above was shown by seeding an aqueous solution with a crystal of the authentic material.

*Methyl*neo*brucidinium chloride* is prepared from the iodide in the usual way by silver chloride. When sulphur dioxide is passed into the dark red filtrate after this has been concentrated on the water-bath under reduced pressure, slightly sticky, yellow needles separate; these are triturated with hot acetone, which causes the compound to crystallise in beautiful prisms. Methyl*neo*brucidinium chloride crystallises from absolute alcohol, in which it is rather readily soluble, in colourless, anhydrous needles, m. p. 188°, which absorb moisture on keeping and then melt at about 163°. On addition of ether to an alcohol–acetone solution, the chloride forms pale yellow, waxy prisms, m. p. 163°, which retain a molecule of water of crystallisation after being heated at 100° (Found: C, 63·9; H, 7·5. $C_{24}H_{31}O_3N_2Cl,H_2O$ requires C, 64·2; H, 7·4%). It dissolves readily in water, and is precipitated unchanged as a rapidly-crystallising oil by 50% potassium hydroxide solution. The colour reactions with ferric chloride in hydrochloric acid are identical with those given by methoxymethyldihydrobrucidine, and are also produced by silver nitrate in dilute nitric acid, whilst the addition of a drop of potassium dichromate to a solution in 60% sulphuric acid develops a yellowish-brown colour which does not alter on standing. After the chloride has been heated with 25% methyl-alcoholic potassium hydroxide on the water-bath for 30 minutes in the usual way, the addition of water precipitates a base, which crystallises from ethyl alcohol in colourless needles, m. p. 115°; the base melts at the same temperature in admixture with methoxy-

methyldihydrobrucidine. The chloride yields methyl-ψ-brucidine when heated (see p. 1652). In order to test the possibility of reducing methyl*neo*brucidinium salts, the sulphuric acid solution obtained directly from methoxymethyldihydrobrucidine was reduced in the usual apparatus for 18 hours with a current of 4·5 amps. The contents of the colourless solution, which began to redden as soon as the current was switched off, were isolated as the iodide in the manner described above. This iodide formed colourless prisms, m. p. 298° (decomp.), which were identical with a very pure specimen of methyl-*neo*brucidinium iodide (Found: C, 55·6; H, 6·0%). The fact that reduction had not taken place was confirmed by converting the corresponding chloride, m. p. 188°, into methyl-ψ-brucidine by heating.

Methyl-ψ-brucidine.—This substance is prepared either (i) from methoxymethyldihydrobrucidine dimethochloride (B) or (ii) from methyl*neo*brucidinium chloride.

(i) Methoxymethyldihydrobrucidine dimethochloride (B) (27 g.), free from inorganic material, is heated gently over a flame in test-tubes in batches of 3 g. until the evolution of methyl chloride and inflammable gas ceases. The clear, glassy residue is dissolved in benzene, the solution filtered from a little charred material, and the solvent distilled; the crystalline solid (16·5 g.), m. p. 194°, thus obtained is recrystallised from ethyl alcohol. Pure *methyl-ψ-brucidine* forms colourless tablets, m. p. 198—199° without decomposition [Found: C, 72·8; H, 7·7; N, 7·4; OMe, 15·7; *M*, in camphor, 430. $C_{24}H_{30}O_3N_2$ requires C, 73·1; H, 7·6; N, 7·1; $(OMe)_2$, 14·9%; *M*, 394]. It is, however, often green, melting at about 196°, but in this condition is sufficiently pure for most purposes. It is insoluble in water, readily soluble in benzene, acetone, and dilute acetic acid, and is stable to boiling 20% potassium hydroxide solution. A solution in dilute sulphuric acid instantly decolorises permanganate, forming the characteristic green solution with the pink tinge which is also produced by ferric chloride in dilute hydrochloric acid or ethyl alcohol. The base is recovered unchanged after being electrolysed in 25% sulphuric acid for 9 hours with a current of 4·5 amps. in the usual apparatus, or after being shaken in cold dilute acetic acid solution in an atmosphere of hydrogen in presence of reduced palladous chloride and gum arabic.

The *dihydriodide*, prepared by adding sodium iodide to a solution of the base in dilute hydrochloric acid, crystallises from water in leaflets, m. p. 259° (decomp.) (Found in material dried at 100°: C, 44·1; H, 4·9. $C_{24}H_{30}O_3N_2,2HI$ requires C, 44·3; H, 4·9%).

The *methiodide* is formed (*a*) directly from methyl-ψ-brucidine, or (*b*) from methoxymethyldihydrobrucidine dimethochloride (B).

(*a*) Powdered methyl-ψ-brucidine (1 g.) and methyl iodide (3 c.c.) react at once in the cold to form a jelly which rapidly crystallises. The methiodide, obtained thus in theoretical yield, separates from methyl alcohol in colourless plates, m. p. 297° (decomp.) (Found: C, 55·8; H, 6·1. $C_{24}H_{30}O_3N_2$,MeI requires C, 55·9; H, 6·1%). Occasionally it crystallises in needles, m. p. 297°, which change slowly into plates in presence of methyl alcohol.

(*b*) The nitrobenzene mother-liquors from the action of boiling nitrobenzene on methoxymethyldihydrobrucidine dimethochloride (B) (compare p. 1645) contain a small quantity of methyl-ψ-brucidine methochloride and also a little methyl-ψ-brucidine, and these are removed separately by extraction first with water and then with dilute hydrochloric acid. The methochloride was not isolated from the aqueous extract, but was converted by sodium iodide into the methiodide. The crystalline solid thus formed crystallised from ethyl alcohol in colourless needles, m. p. 297° (decomp.) (Found: C, 56·1; H, 6·2%).

The identity of these two specimens of the methiodide was shown by causing a solution of (*b*) in methyl alcohol to deposit plates on seeding with (*a*), and also by seeding an ethyl-alcoholic solution of (*a*) with (*b*), when the methiodide separated in needles.

The Formation of a By-product by the Action of Heat on Methoxymethyldihydrobrucidine Dimethochloride (*B*).—When the dimethochloride is contaminated by inorganic matter, *e.g.*, sodium chloride if the silver chloride used in its formation has been prepared from sodium chloride, the yield of methyl-ψ-brucidine is lowered, pyridine bases are formed during the heating, and a *by-product* is obtained. For example, the dimethochloride (30 g.), containing some sodium chloride, yielded a benzene extract containing pure methyl-ψ-brucidine (10 g.) together with a residue insoluble in benzene (4 g.). The investigation of this substance is at present in progress and the results already obtained show that we have encountered here an important degradation by fission of the brucine molecule.

Methyl-ψ-brucidine (ii). This base is also obtained by heating methyl*neo*brucidinium chloride in an oil-bath at 200—210° until effervescence ceases. The dark brown glass is dissolved in dilute acid, and the base is precipitated by potassium hydroxide and crystallised from ethyl alcohol. It forms tablets, melting, either alone or mixed with an authentic specimen of methyl-ψ-brucidine, at 198°.

Permanganate Oxidation of Methyl-ψ-brucidine.

Brucidone Semicarbazone.—Powdered potassium permanganate (6·8 g.: 5 atoms of oxygen) is added gradually to methyl-ψ-brucidine (5 g.) in ice-cold, mechanically-stirred acetone (500 c.c.); the colour

of the permanganate disappears slowly, and oxidation seems to be complete at the end of the addition. The manganese precipitate is filtered off, but yields no solid product. Removal of the acetone leaves a pale yellow, gummy residue (4 g.), which has not been obtained crystalline, and which yields only oily products when heated with methyl-alcoholic potassium hydroxide, or when dissolved in concentrated sulphuric acid (compare strychnidone, this vol., p. 1615). It is therefore converted into the semicarbazone by boiling a solution of the gum, semicarbazide hydrochloride (3·4 g.), and potassium acetate (3·4 g.) in aqueous alcohol under reflux for 1½ hours. Water is added, the alcohol distilled off under reduced pressure, and the crystalline precipitate, which forms during the distillation, is recrystallised from ethyl alcohol, being obtained in colourless needles which shrink at 210° and evolve gas at 226°, without complete fusion (loss at 100°, 13·1. 1½EtOH requires loss, 12·8%. Found in dried material: C, 60·8; H, 7·0; N, 15·1. $C_{24}H_{31}O_5N_5$ requires C, 61·4; H, 6·6; N, 14·9%). This *semicarbazone* is very sparingly soluble in cold methyl or ethyl alcohol. From the analyses, it appears to be the monosemicarbazone of a ketone derived from methyl-ψ-brucidine by the loss of CH_2 and its replacement by O, and the further introduction of one oxygen atom.

The unsharp melting point suggested that this material might be a mixture, and fruitless efforts were made to obtain pure components by repeated crystallisation from methyl or ethyl alcohol. The melting point remained unaltered. Purification was also attempted by extracting the substance with boiling methyl alcohol in sufficient quantity to dissolve only half, filtering the hot solution from the residue *A*, allowing it to deposit a second fraction *B* on cooling, and obtaining a third fraction *C* when the mother-liquor had remained over-night. *A* was recrystallised, and the mother-liquor yielded a very small fraction, *D*, on standing over-night. These fractions all formed colourless needles, which were dried in a vacuum desiccator, and the analyses agreed well with the formula already suggested (see below). On the other hand, the specimens differ in melting point and contain different amounts of solvent of crystallisation. (*A*) shrinks at 200°, melts at 220—225° (decomp.), and is not changed by recrystallisation (loss at 100°, 2·3. ½MeOH requires loss, 3·3%. Found in material dried at 100°: C, 62·0; H, 6·5%). (*B*) shrinks at 245°, melts at 257° (decomp.), and is not changed by recrystallisation (loss at 100°, 11·4. 2MeOH requires loss, 12·0%. Found in dried material: C, 61·6; H, 6·6%). (*C*) shrinks at 200° and melts at 235° (decomp.); there was not enough for recrystallisation (loss at 100°, 7·5. 1MeOH requires loss, 6·4%. Found in dried material: C, 61·4; H, 6·7%). (*D*), only

0·0327 g., shrinks at 195° and melts at 245° (decomp.) (loss at 100°, 10·4%. Found in dried material: C, 59·7; H, 6·5%).

It is possible that brucidone is a mixture of isomerides or that the semicarbazone group introduces geometrical isomerism.

Methoxymethyltetrahydrobrucidine.—A solution of methoxymethyldihydrobrucidine (20 g.) in sulphuric acid (200 c.c. of 20%) is reduced in the usual apparatus for 16 hours with a current of 5 amps., the temperature being kept at 18° by cooling in water. The methoxymethyldihydrobrucidine may be used in the crude condition in which it is obtained when water is added to the product of the interaction of brucidine methosulphate and methyl-alcoholic potassium hydroxide. After the reduction, excess of ammonia (*d* 0·880) is added while the liquid is stirred and cooled in ice; the product is thus obtained as a finely divided solid, whereas precipitation without cooling yields a caseous mass which solidifies to a single hard lump. The precipitate is collected, washed, dried (18 g.), and crystallised from methyl alcohol, from which it separates in colourless needles (Found: C, 70·2; H, 8·3. $C_{25}H_{36}O_4N_2$ requires C, 70·0; H, 8·4%).

Methoxymethyltetrahydrobrucidine melts at 133—135° and distils without decomposition at 253°/2 mm. It is somewhat soluble in the usual solvents and crystallises in beautiful needles from light petroleum (b. p. 60—80°). It dissolves readily in dilute acetic or mineral acid, and does not redden on exposure nearly so quickly as methoxymethyldihydrobrucidine. Acetic anhydride seems to be without action; after the mixture has been boiled for a few minutes and water and excess of ammonia have been added, the base is recovered unchanged.

The *dihydriodide* is prepared by adding concentrated sodium iodide solution to a solution of the base in 2*N*-sulphuric acid. On scratching, the dihydriodide separates in practically quantitative yield; it crystallises from water in colourless needles, which melt at 212° to a yellow froth (Found: I, 37·3. $C_{25}H_{36}O_4N_2,2HI$ requires I, 37·1%). It is sparingly soluble in ethyl alcohol, and becomes yellow on keeping.

When a hot aqueous solution of the dihydriodide is treated with excess of silver chloride, and the filtrate is evaporated to dryness under reduced pressure on the water-bath, the *dihydrochloride* is obtained as a colourless glass, which crystallises when ether is added carefully to a solution in alcohol–acetone. It forms rectangular plates, which are very soluble in water and evolve gas at 150° without melting completely. The residue is probably methyl*neo*-dihydrobrucidinium chloride, which is produced when the dihydrochloride is decomposed in boiling mesitylene (b. p. 165°) (see p. 1659).

The *methiodide* (*A*) is prepared by heating the base (4 g.) and methyl iodide (5 c.c.) under reflux on the water-bath for 20 minutes; a crystalline precipitate is soon formed. The methyl iodide is distilled away, and the residue separates from ethyl alcohol in colourless leaflets (Found: C, 54·9; H, 7·2. $C_{25}H_{36}O_4N_2$,MeI requires C, 54·7; H, 6·8%). The methiodide dissolves rather readily in water. It melts at 166—167°, losing methyl iodide quantitatively (loss in an oil-bath at 165—170°, 24·9. $C_{25}H_{36}O_4N_2$,MeI requires loss, 24·9%), and regenerating the base, m. p. 134°, which was identified by the mixed melting-point method.

The *methochloride* (*A*), prepared in the usual way from the methiodide and silver chloride, forms a glassy mass. When it was heated with an excess of methyl-alcoholic potassium hydroxide at 120° for 1 hour, and water was added, methoxymethyltetrahydrobrucidine was regenerated, and identified by the mixed melting-point method.

The *methiodide* (*B*) is obtained by heating either (i) the dimethiodide (A) (p. 1658) or (ii) the dimethiodide (B) (p. 1656).

(i) When methoxymethyltetrahydrobrucidine dimethiodide (A) is heated in an oil-bath at 230°, it melts and evolves methyl iodide quantitatively. The glassy residue crystallises from ethyl alcohol in flattened needles or leaflets, m. p. 298° (decomp.) (Found: C, 54·9; H, 6·7. $C_{25}H_{36}O_4N_2$,MeI requires C, 54·7; H, 6·8%). This substance is sparingly soluble in ethyl alcohol and in water and crystallises from the latter in characteristic prisms, m. p. 298° (decomp.), which become chalky when dried in a vacuum desiccator.

(ii) Methoxymethyltetrahydrobrucidine dimethiodide (B) (1 g.) is heated gently in a test-tube over a flame until the evolution of methyl iodide ceases. If the heating becomes too vigorous, deep-seated decomposition takes place, and gases are evolved which burn with a luminous flame, partly condense on the cold part of the tube, and smell strongly of pyridine bases. The residue is crystallised from ethyl alcohol, and this purification is repeated if necessary until leaflets, m. p. 298° (decomp.), are obtained. This *methiodide* (*B*) separates from water in colourless, characteristic prisms, m. p. 298° (decomp.) (Found: C, 55·1; H, 6·9; I, 22·4. $C_{25}H_{36}O_4N_2$,MeI requires I, 22·3%). The identity of the specimens of the methiodide (B) obtained from the dimethiodides (A) and (B) was shown by seeding an aqueous solution prepared in one way with a crystal prepared in the other way.

The *methochloride* (*B*), prepared in the usual way from the methiodide and silver chloride, forms a colourless glass. When this is heated in a test-tube over a flame, it decomposes before methyl

chloride is split off, and no methyldihydrobrucidine can be isolated from the charred residue. When exposed to water vapour in a bell-jar, the glassy methochloride crystallises in sticky needles, which after being pressed on porous tile and dried in a vacuum desiccator, decompose without melting at about 210.°

Methoxymethyltetrahydrobrucidine Dimetho-salts.

The Dimethosulphates (A) and (B).—Methoxymethyltetrahydrobrucidine reacts with methyl sulphate even more slowly than does methoxymethyldihydrobrucidine. In this case no monomethosulphate has been isolated. A solution of dried methoxymethyltetrahydrobrucidine (46 g.) and pure methyl sulphate (100 c.c.) in dry benzene (300 c.c.) is boiled on the water-bath under reflux for 24 hours, carefully protected from moisture. The hot benzene is decanted, but the residual mixture of brown gum and needles (90 g.) still retains some methyl sulphate and a little solvent, even after being washed as thoroughly as possible with benzene, which is then blown away in a current of air. This mixture must contain two dimethosulphates, (A) and (B), since it is converted into two dimethiodides, but attempts to isolate the dimethosulphates have been fruitless, and the mixture is therefore converted into the dimethiodides (A) and (B) by sodium iodide.

The *dimethiodide* (*B*) is prepared by adding sodium iodide (100 g.) in warm water (40 c.c.) to a warm solution of the above mixture of dimethosulphates in water (60 c.c.). On cooling and scratching, crystallisation begins, and after 24 hours the solid is collected, washed with water, and dried in a vacuum (31 g.). (The mother-liquors contain the dimethiodide A together with a small quantity of the dimethiodide B, and their investigation is described on p. 1658.) One recrystallisation from water (filter : see below) is usually sufficient for the purification of this product, although on a few occasions it had an unpleasant smell, which was first removed by grinding with cold ethyl alcohol. The dimethiodide (B) crystallises from water in prismatic needles, m. p. 287° (decomp.) (Found : C, 45·3, 45·4; H, 5·5, 5·7. $C_{25}H_{36}O_4N_2,2MeI$ requires C, 45·5; H, 5·9%). It is sparingly soluble in cold water or methyl or ethyl alcohol, but dissolves readily in hot water. When an aqueous solution is saturated with sulphur dioxide, a yellow oil is formed which crystallises on standing. This additive product, which contains sulphur dioxide, is very sparingly soluble in cold water, but readily forms an orange solution on warming, which evolves sulphur dioxide when boiled and then becomes colourless. When the colourless solution is cooled, the dimethiodide separates in a pure condition. The dimethiodide is very stable to alkali, and was

recovered in good yield after being heated with a large excess of 25% methyl-alcoholic potassium hydroxide at 140° for 30 minutes.

The crude precipitate of the dimethiodide is usually mixed with a small quantity of an ochreous, amorphous substance, which remains undissolved on recrystallisation of the precipitate from water. The amount of this by-product increases to about one-tenth of the weight of the dimethiodide if the solutions of the dimethosulphates and sodium iodide are boiling when mixed. The insoluble solid from the recrystallisation of the dimethiodide (see above) is crystallised fom methyl alcohol, in which it is very sparingly soluble, by dissolving it in much boiling solvent (charcoal), concentrating the solution until crystallisation begins, and allowing it to cool. The substance thus obtained in purple-red, glistening prisms melts at 230° (decomp.) and is a *periodide* of the dimethiodide (B) (Found: I, 55·6. $C_{25}H_{36}O_4N_2,2MeI,I_2$ requires I, 52·6%). This periodide is slowly decomposed by boiling water; it is stable to cold dilute nitric acid, but is instantly decomposed on boiling, iodine being liberated. When sulphur dioxide is passed into an aqueous suspension, the crystals change into a red gum, which is collected, and boiled with water until the solution becomes colourless and the smell of sulphur dioxide is no longer perceptible; on cooling, the dimethiodide (B) separates in colourless prisms, m. p. 287°.

The *dimethochloride* (*B*) is prepared by heating an aqueous solution of the dimethiodide (B) with excess of silver iodide, and evaporating the filtrate to dryness on the water-bath under reduced pressure. The colourless, crystalline mass thus obtained separates from ethyl alcohol in plates which melt to a froth and lose solvent at 138°, after drying in a vacuum desiccator. On further heating, the froth hardens and melts at 214°. After drying at 100°, the dimethochloride has m. p. 214° (decomp.) (loss at 100°, 8·5. 1EtOH requires loss, 8·0%. Found in dried material: Cl, 13·7. $C_{25}H_{36}O_4N_2,2MeCl$ requires Cl, 13·4%).

The dimethochloride loses a molecule of methyl chloride when it melts at 214°, forming methoxymethyltetrahydrobrucidine methochloride (B). After heating at 245° in an oil-bath until the evolution of methyl chloride ceased, the residual glass, consisting of the methochloride (B), was converted into the methiodide by adding sodium iodide to an aqueous solution, and crystallising the precipitate from water. The methiodide (B) separated in the characteristic prisms, m. p. 298° (decomp.), which became chalky on drying (Found: C, 54·5; H, 6·8%).

When the dimethochloride was heated in a test-tube at 300°, further decomposition took place. No methyl-ψ-dihydrobrucidine could be isolated from the residue, which consisted only of charred material.

if the heating was sufficiently prolonged to allow complete elimination of the methyl chloride.

The *dimethiodide* (*A*) is obtained either (i) from the mother-liquors of the preparation of the dimethiodide (B), or (ii) by the direct combination of the base and methyl iodide.

(i) The mother-liquors from the preparation of the dimethiodide (B) (p. 1656) are mixed with 50% potassium hydroxide solution; a caseous mass then separates, and soon hardens sufficiently to be pressed between porous tiles in order to remove as much alkali as possible. On boiling with a little ethyl alcohol, it becomes colourless and completely crystalline, without passing into solution to any great extent. The crystals are collected after several hours, washed with alcohol, and dried in a vacuum desiccator (33 g.). This product is essentially the dimethiodide (A), but contains also a little of the dimethiodide (B). In the first experiment, these were separated by fractional crystallisation from methyl alcohol, but later, when the properties of the dimethiodide (A) became known, the following process was found to be much more satisfactory. The mixture is dissolved in a little boiling water, and the solution is cooled, seeded with the dimethiodide (B), and set aside over-night. The remainder of the dimethiodide (B) separates in a practically pure state, and is collected, washed, and dried (5 g.). The filtrate now contains the dimethiodide (A), which is very soluble in water. It is saturated with sulphur dioxide while stirred continuously, and the yellow, crystalline additive compound which is formed is collected, washed with a little sulphurous acid, and dissolved in boiling methyl alcohol. After boiling for about 15 minutes, the solution becomes colourless, and is then concentrated to about 100 c.c. On cooling, the *dimethiodide* (*A*) crystallises in an almost pure condition, m. p. 230° (25 g.). (The yield of the combined dimethiodides A and B is about 81% of that theoretically possible.) One recrystallisation from methyl alcohol gives the pure product in stout prisms, which melt at 230—232° to a colourless froth (see below) (Found: C, 45·1; H, 5·8. $C_{25}H_{36}O_4N_2,2MeI$ requires C, 45·5; H, 5·9%). It dissolves readily in cold water, but only very sparingly in methyl or ethyl alcohol. When it is heated at its melting point, a molecule of methyl iodide is liberated smoothly; the glassy residue crystallises from water in the characteristic prisms of the methiodide (B) (see p. 1655).

(ii) A preliminary experiment showed that methoxymethyltetrahydrobrucidine combines with only one molecule of methyl iodide at 100°, even when heated for long periods. When, however, the base (5 g.) and methyl iodide (10 c.c.) are heated in a sealed tube at 140° for 24 hours, and the methyl iodide is distilled off, the

residual solid is the *dimethiodide* (*A*). After two recrystallisations from methyl alcohol, it forms stout prisms, m. p. 230°, which are identical in every way with the substance described above (Found: C, 45·6; H, 6·0; I, 35·4. $C_{25}H_{36}O_4N_2$,2MeI requires I, 35·7%).

The *dimethochloride* (*A*), prepared from the dimethiodide in the usual way by silver chloride, forms a colourless glass which cannot be crystallised. When it is heated gently in a test-tube over a flame, methyl chloride is evolved smoothly; the colourless residue, crystallised from methyl alcohol, forms needles, melting, either alone or when mixed with a specimen of methoxymethyltetrahydrobrucidine, at 133°.

*Methyl*neo*dihydrobrucidinium Salts.*

Methoxymethyltetrahydrobrucidine is not attacked by boiling 10% sulphuric acid under the conditions in which methoxymethyldihydrobrucidine yields methyl*neo*brucidinium sulphate. After the acid solution had been boiled for 2½ hours, ammonia precipitated 98% of the base used. Nor were successful results obtained when methoxymethyltetrahydrobrucidine dihydriodide or dihydrochloride was heated in a test-tube, since a much wider decomposition evidently took place. Ultimately, however, it was found possible to obtain the iodide in the following way.

The iodide. A suspension of methoxymethyltetrahydrobrucidine dihydrochloride (5 g.) in mesitylene (40 c.c.) is heated in an oil-bath at 180°. The solid becomes gummy and evolves hydrogen chloride, which is blown away from time to time in a current of air. After 20 minutes, the light brown gum hardens and is broken up, and the heating is continued for 10 minutes more in order to ensure complete decomposition. Ether is added to the cooled product, and the glassy solid is collected and dried at 100° (3·9 g.). Attempts to crystallise this chloride were unsuccessful (compare below), and it was therefore converted into the iodide. A solution of the chloride in water (25 c.c.) is saturated with sulphur dioxide, and concentrated sodium iodide is added drop by drop until no more oil separates. This additive product solidifies after a short time, and the orange mass thus obtained is boiled with water until the smell of sulphur dioxide has disappeared. On cooling, *methyl*neo*dihydrobrucidinium iodide* (3 g.) separates; it crystallises from water in colourless bipyramids, m. p. 283° (decomp.) (Found: C, 54·9; H, 6·4. $C_{24}H_{33}O_3N_2I$ requires C, 55·0; H, 6·3%). It is rather sparingly soluble in cold water or ethyl alcohol and crystallises in plates from the latter. An aqueous solution is not precipitated by ammonia or dilute alkali solution; concentrated potassium hydroxide solution precipitates the iodide unchanged.

The *chloride*, prepared by heating an aqueous solution of the

iodide with silver chloride and evaporating the filtrate under reduced pressure on the water-bath, is a colourless glass which does not crystallise. An aqueous solution is not precipitated by ammonia or dilute alkali solution. On heating in a test-tube over a flame, charring occurs very readily; the residue dissolves in water to a red solution, which becomes deep red on addition of ammonia, and then bright green on addition of a few drops of potassium hydroxide; much concentrated potassium hydroxide solution precipitates a green oil, which has not been examined. No methyl-ψ-dihydrobrucidine is formed.

Methoxymethyltetrahydrobrucidine Dimethohydrogencarbonates (A) and (B) and their Decomposition by Heat. Methyl-ψ-dihydrobrucidine.

The Dimethohydrogencarbonate (*A*).—This substance is prepared by shaking a hot aqueous solution of methoxymethyltetrahydrobrucidine dimethiodide (A) with an excess of either silver hydroxide or silver carbonate. In either case, the alkaline filtrate is evaporated as far as possible in an open basin on the water-bath, and then left in a vacuum desiccator over-night. The gummy residue crystallises on being rubbed with acetone containing a little ethyl alcohol, and is recrystallised by the cautious addition of ether to an ethyl-alcoholic solution. The *dimethohydrogencarbonate* (*A*) forms almost colourless, hygroscopic crystals, m. p. 92—94°, or 103—104° when heated in a sealed capillary tube (Found in material dried in a vacuum desiccator: C, 52·5; H, 8·3. $C_{25}H_{36}O_4N_2,2MeHCO_3,5H_2O$ requires C, 51·9; H, 8·1%). It is very soluble in water or ethyl alcohol, and evolves carbon dioxide on treatment with dilute hydrochloric acid. When a small quantity is heated gently in a test-tube over a flame, carbon dioxide is eliminated; the light brown, glassy residue crystallises from methyl alcohol in colourless needles, which, either alone or when mixed with methoxymethyltetrahydrobrucidine, melt at 134°.

The *dimethohydrogencarbonate* (*B*) is prepared from the dimethiodide (B) exactly in the manner described above in the case of the isomeride (A). It is crystallised by the careful addition of ether to a filtered solution in ethyl alcohol, and forms colourless prisms, which are hygroscopic and melt at 109° after drying in a vacuum desiccator (Found: C, 50·3; H, 8·3. $C_{25}H_{36}O_4N_2,2MeHCO_3,6H_2O$ requires C, 50·6; H, 8·1%). It is very soluble in water or ethyl alcohol, and evolves carbon dioxide on treatment with acids.

When it is heated at 135° in an oil-bath, carbon dioxide is evolved. The heating is continued for 30 minutes until the frothing has ceased, and the clear, glassy residue is dissolved in water. As the solution gives no precipitate with ammonia and evolves carbon dioxide on

treatment with acids, it must contain a methohydrogencarbonate. Sodium iodide is therefore added; the precipitate formed crystallises from water in colourless prisms, m. p. 298°, and is identical with methoxymethyltetrahydrobrucidine methiodide (B). The product of the decomposition is therefore the *methohydrogencarbonate* (*B*).

Methyl-ψ-dihydrobrucidine. The dimethohydrogencarbonate (B) (1 g.) is heated gently in a test-tube over a flame. It melts to a froth while gradually losing carbon dioxide, and the methyl alcohol which is evolved may be burnt at the mouth of the tube; when the effervescence has ceased, the light brown residue is quite mobile. After cooling, the tubes are broken and the contents extracted with boiling ethyl alcohol. The filtrate is concentrated to small volume; *methyl-ψ-dihydrobrucidine,* which then separates in moderate yield, recrystallises from ethyl alcohol in colourless tablets, m. p. 220—221° [Found: C, 72·5; H, 8·2; OMe, 15·8. $C_{24}H_{32}O_3N_2$ requires C, 72·7; H, 8·1; $(OMe)_2$, 15·6%]. This substance is soluble in dilute hydrochloric or acetic acid; it is sparingly soluble in ethyl alcohol, moderately easily soluble in acetone, and dissolves readily in benzene. It is extremely stable to oxidation by permanganate in acetone.

The *dihydriodide*, prepared by the addition of sodium iodide to a solution of the base in dilute hydrochloric acid, crystallises from water in small, wart-like granules, which melt at 215—217° to a yellow froth (Found in material dried at 100°: C, 44·0; H, 5·2. $C_{24}H_{32}O_3N_2,2HI$ requires C, 44·2; H, 5·2%). It separates from ethyl alcohol in stout prisms, and is sparingly soluble in this solvent and in water.

Colour Reactions of the Brucidine Derivatives.

The most useful reaction is that with ferric chloride in dilute hydrochloric acid, and a positive result is a deep green or bluish-green coloration, pink in thin layers, becoming red on boiling; when the reaction is negative, no colour is produced even on heating. The following substances give the reaction: brucidine, brucidine methosulphate, tetrahydrobrucine and its methochloride, methoxymethyldihydrobrucidine and its methochloride (B), methoxymethyltetrahydrobrucidine and its methochloride (B), methyl-ψ-brucidine and its methochloride prepared by either method, methyl*neo*brucidinium chloride, methyl-ψ-dihydrobrucidine, and methyl*neo*dihydrobrucidinium chloride. The substances which do not give the reaction are: methoxymethyldihydrobrucidine methosulphate (A) and methochloride (A), methoxymethyltetrahydrobrucidine methochloride (A), methoxymethyldihydrobrucidine dimethochlorides (A) and (B), methoxymethyltetrahydrobrucidine dimethochlorides (A) and (B), dioxymethoxymethyldihydrobrucidine (Y) methochloride, and

as already mentioned, brucine itself.* Since both strychnidine and brucidine give characteristic but entirely different ferric chloride reactions, the latter must be concerned with the only part of the molecule which is not identical in the two substances, namely, the aromatic nucleus, and this view is confirmed in the case of strychnidine by the observation that those derivatives which give a negative or feeble ferric chloride reaction are the only strychnidine derivatives which do not couple with diazonium salts. It then becomes apparent that the occurrence of the reaction in a particular case is dependent on the condition of the nitrogen atom bound to the aromatic nucleus. When this is salt-forming, the reaction is positive, whilst a negative reaction is due to its inclusion in the group –N–CO– as in brucine, or in a quaternary ammonium salt grouping as in the various dimethochlorides (and dihydrochlorides) described in this and the preceding communications. These views are in complete harmony with experience of simpler aromatic amine derivatives; thus dimethylaniline couples with diazonium salts, whereas *N*-methylacetanilide and phenyltrimethylammonium chloride do not. It is on this basis that we have allocated formulæ to the methochlorides (A) and (B) of methoxymethyldihydrobrucidine and methoxymethyltetrahydrobrucidine respectively (see pp. 1630 and 1633) and have drawn the important inference that the conversion of brucidine into methoxymethyldihydrobrucidine is accompanied by a transposition of the function of the nitrogen atoms in respect of their basic character.

The dichromate test in 60% sulphuric acid is of inferior diagnostic value. It is given by all the brucidine derivatives, but the green colour appears much more slowly in the cases where the ferric chloride reaction is negative.

We are indebted to Mr. R. I. E. Hall, M.A., for preparing the large quantities of material required in these two researches and also to Mr. F. Hall for carrying out, with his usual skill, the whole of the analyses. One of us (W. H. P.) is indebted to the Government Grant Committee of the Royal Society for repeated grants which have covered much of the expense of these investigations.

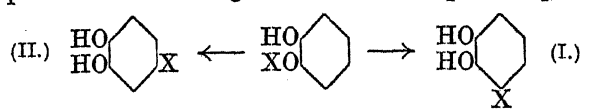
UNIVERSITIES OF OXFORD AND
MANCHESTER. [*Received, May 24th*, 1927.]

* The brucidine derivatives do not exhibit the reaction in concentrated hydrochloric acid solution. In the cases when the reaction is positive, however, the colour appears on dilution, and this behaviour is clearly due to the formation and hydrolysis of dihydrochlorides.

CCXII.—*A Synthesis of Safrole and o-Safrole.*

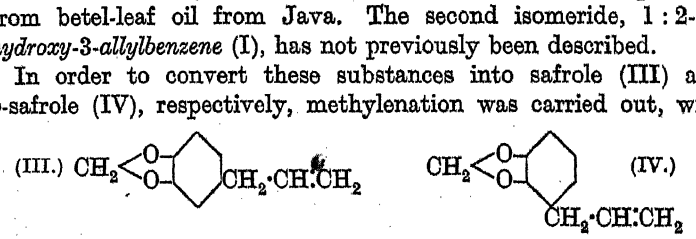
By WILLIAM HENRY PERKIN, jun., and VICTOR MARTIN TRIKOJUS.

No direct synthesis of safrole has been recorded, the most recent attempt being that of Baker and Robinson (J., 1925, **127**, 1424), who distilled the product of the action of silver oxide and water upon γ-piperonylpropyltrimethylammonium iodide, but obtained *iso*safrole, the double bond moving into the position of greater stability. Kawai (*Sci. Papers Inst. Phys. Chem. Res.*, 1925, **3**, 263) has shown that the monoallyl ether of pyrocatechol undergoes the Claisen rearrangement to give an oil which he considered to be a mixture of 3- and 4-allyl-1 : 2-dihydroxybenzene, the change taking place in the following manner (X = $CH_2{\cdot}CH{:}CH_2$) :



This matter has now been reinvestigated and, by repeated fractionation of the product of the rearrangement, both of the above isomerides have been isolated in a pure state as colourless, crystalline solids melting at 28° and 48° respectively. As further confirmation of the course of the Claisen migration, it has been found that the properties of the higher-melting isomeride (II) are in accord with those assigned to the "4-allylbrenzcatechin" which Schimmel and Co. (*Centr.*, 1907, II, 1741) isolated in small quantity from betel-leaf oil from Java. The second isomeride, 1 : 2-*dihydroxy*-3-*allylbenzene* (I), has not previously been described.

In order to convert these substances into safrole (III) and *o*-safrole (IV), respectively, methylenation was carried out, with



moderately good yields, by gently refluxing them with methylene iodide and anhydrous potassium carbonate in dry acetone solution. By employing such mild conditions, any change into the isomeric *iso*safroles during the course of the reaction was inhibited. The identity of the synthetic product with naturally occurring safrole has been established by preparing the pentabromo-derivative (m. p. 169°) and the acetamido-derivative (m. p. 162—163°) and comparing these with the same derivatives from natural safrole. The properties of the hitherto unknown isomeride *o-safrole* (IV)

(which resembles safrole in odour and in many other ways) have been recorded.

The process of methylenation described above takes place very smoothly without formation of tarry products and may prove to be valuable in other cases of this kind.

EXPERIMENTAL.

Mono- and Di-allyl Ethers of Pyrocatechol.—Pyrocatechol (132 g.) and pure allyl bromide (144 g.) were dissolved in pure dry acetone (220 c.c.), finely powdered, freshly heated potassium carbonate (170 g.) was added gradually with constant shaking, and the whole refluxed for 6—8 hours on the water-bath, the condenser being fitted with a calcium chloride tube (compare Kawai, *loc. cit.*). After removal of the acetone, addition of water and dilute sulphuric acid, and extraction with ether, the monoallyl ether and unchanged pyrocatechol were removed by washing the extract with dilute alkali solution, and the ethereal solution was then dried with anhydrous sodium sulphate and evaporated. The yield of pure diallyl ether was 43 g. (b. p. 124—125·5°/13 mm.). The alkali washings were immediately acidified and the oil was taken up in chloroform. After being repeatedly washed with water to remove pyrocatechol, the chloroform was evaporated and the oil distilled, yielding 90 g. of pure monoallyl ether, b. p. 107·5—109°/15 mm. The yields of both ethers were considerably higher than those recorded by Kawai under almost analogous conditions.

Molecular rearrangement. The monoallyl ether (92 g.) was heated in a flask, fitted with a ground-in condenser, in a paraffin bath at 170—180°; the inner temperature suddenly rose to 265° with momentary boiling, the colour of the liquid changing to red. After cooling, the product was fractionated under 15—16 mm. and fractions, b. p. 142—152° (66·2 g.) and 152—160° (17·2 g.), were collected, leaving a resinous, non-volatile residue (9 g.). The second fraction solidified on standing and consisted chiefly of 1 : 2-dihydroxy-4-allylbenzene, melting at 40—41° with previous softening. Kawai noticed the formation of some crystals in his higher fraction (b. p. 155—160°/16 mm.) and suggested that they were due to pyrocatechol which had been set free during the rearrangement (compare Claisen, *Annalen*, 1913, **401**, 21). In the present instance, however, no pyrocatechol was observed and it is probable that his crystals were those of 1 : 2-dihydroxy-4-allylbenzene.

After repeated systematic refractionation of the above two fractions, both isomerides were isolated in a pure condition, the proportion of 1 : 2-dihydroxy-3-allylbenzene to its isomeride in the rearranged product being approximately 5 to 4.

1 : 2-*Dihydroxy*-4-*allylbenzene* (II) is a colourless, waxy, crystalline solid soluble in water and most other solvents, but sparingly soluble in petroleum. It forms colourless needles, m. p. 48°, from benzene–light petroleum and boils at 147—149°/10 mm. and at 156—158°/16 mm. (Found: C, 72·1; H, 6·8. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). The dibenzoyl derivative (Schotten-Baumann) separates from light petroleum in colourless prisms, m. p. 71°. These properties clearly indicate that the substance is identical with the "allylbrenzcatechin" isolated from Java betel-leaf oil (*loc. cit.*).

1 : 2-*Dihydroxy*-3-*allylbenzene* (I) is best purified by distillation under reduced pressure and has b. p. 143·5—145°/15 mm. If allowed to crystallise slowly, it separates in large, colourless, flat prisms, m. p. 28°, but it has a tendency to remain liquid below this temperature. Owing to this property, it was not found possible to recrystallise it satisfactorily. It dissolves readily in most solvents except petroleum, whilst in water it is not as soluble as its isomeride (Found: C, 72·1; H, 6·5. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

It resembles its isomeride in having a phenolic odour and in aqueous solution it gives with ferric chloride an olive-green colour, changing to wine-red on addition of sodium carbonate.

The *dibenzoyl* derivative separates from light petroleum in colourless prisms, m. p. 60—61° (Found: C, 77·1; H, 5·2. $C_{23}H_{18}O_2$ requires C, 77·1; H, 5·0%).

Safrole (III).—1 : 2-Dihydroxy-4-allylbenzene (10 g.) and methylene iodide (18 g.) were dissolved in pure dry acetone (35 c.c.) and finely powdered, freshly ignited potassium carbonate (20 g.) was gradually added with shaking to prevent caking. After gently refluxing on the water-bath for 12 hours, the acetone was removed, the product was made acid with dilute sulphuric acid and extracted with ether, and the ethereal solution was repeatedly washed with dilute aqueous sodium hydroxide and finally with water, dried over sodium sulphate, and evaporated. On carefully distilling the residue under reduced pressure, methylene iodide first passed over; when this had been completely removed, a fraction, b. p. 100—101·5°/10—11 mm., consisting of 2·5 g. of a clear, colourless oil, was collected. This was identified as safrole by its characteristic odour and by preparing its *pentabromo*-derivative by gradually adding excess of bromine below 0° and allowing the mixture to stand for some hours; the solid substance which had separated, after recrystallising from ethyl alcohol, melted at 169°, and a mixed melting point with the derivative prepared from ordinary safrole showed no depression. The oil had $n_D^{20°}$ 1·5381 (Found: C, 74·2; H, 6·4. Calc. for $C_{10}H_{10}O_2$: C, 74·1; H, 6·2%). As an additional

proof of identity, 1·35 g. of the synthetic substance were nitrated under the conditions laid down by Foulds and Robinson (J., 1914, **105**, 1963), the nitro-derivative was reduced with tin and hydrochloric acid, and the crude 6-aminosafrole acetylated; the acetyl derivative crystallised from methyl alcohol in colourless needles, m. p. 162—163° (Found: C, 65·5; H, 6·0. Calc. for $C_{12}H_{13}O_3N$: C, 65·7; H, 5·9%), and a mixed melting-point determination with the corresponding derivative from naturally occurring safrole showed no depression.

o-Safrole (IV).—1 : 2-Dihydroxy-3-allylbenzene (20 g.), methylene iodide (36 g.), potassium carbonate (40 g.), and acetone (70 c.c.) were gently refluxed for 14 hours, and the product was treated in a manner similar to that described above in the synthesis of safrole. Methylene iodide was removed under reduced pressure, and the remainder (boiling over 1·5°) collected separately. Yield, 7 g. It was redistilled and collected at 102·5—103°/13 mm. (Found: C, 74·3; H, 6·2. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2%). It boils at 106—107°/16 mm. and at 226—227°/762 mm.

o-Safrole is a colourless, mobile oil which does not crystallise at −20° and has $n_D^{20°}$ 1·5359. It has an agreeable odour, similar to, but not so pronounced as, that of safrole (compare the respective odours of *o*-piperonal and piperonal; Perkin and Trikojus, J., 1926, 2927). On the addition of excess of bromine to *o*-safrole cooled below 0°, a vigorous reaction occurs; the product, which solidifies on standing over-night, is washed with ethyl alcohol and crystallised from the same solvent, in which it is only sparingly soluble. The resulting *pentabromo*-derivative separates in colourless prisms, m. p. 154°, and the yield is almost quantitative (Found: Br, 71·8. $C_{10}H_7O_2Br_5$ requires Br, 71·6%).

One of us (V. M. T.) is indebted to the Royal Commissioners of the 1851 Exhibition for a scholarship which enabled him to take part in this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD.

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CCXIII.—*Monothioethylene Glycol. Part III. Nitrophenyl Thioethers.*

By GEORGE MACDONALD BENNETT and WILLIAM AMBLER BERRY.

IN continuation of the examination of monothioethylene glycol and its derivatives (J., 1921, **119**, 1860; 1922, **121**, 2139), we have now prepared the three isomeric nitrophenyl β-hydroxyethyl

sulphides and a number of related substances. The direct conversion of the parent mercaptan into each of these nitrophenyl thioethers was realised, the *o*-isomeride being obtained in good yield by the action of *o*-bromonitrobenzene and alcoholic potassium hydroxide, and the *m*- and *p*-isomerides by the action of the respective nitrobenzenediazonium salts (compare Stadler, *Ber.*, 1884, **17**, 2073). The most economical method for preparing each of these substances is, however, by the action of ethylene chlorohydrin upon the salt of the nitrothiophenol. The corresponding *p*-nitrobenzyl thioether was obtained in a similar manner from *p*-nitrobenzyl mercaptan, the preparation of which has been improved. The isomeric *p*-nitrophenyl γ-hydroxypropyl sulphide is also described.

From these hydroxy-sulphides, the chloro-, bromo-, and iodosulphides have been produced by known methods. The replacement of the hydroxyl group by chlorine was appreciably less easy in *p*-nitrophenyl γ-hydroxypropyl sulphide than in the β-series (compare Bennett and Hock, J., 1925, **127**, 2671; this vol., p. 477).

The isolation of three of these compounds has been announced by other authors during the course of our work—*o*-nitrophenyl β-chloroethyl sulphide by Lecher and Simon (*Ber.*, 1925, **58**, 409) and *p*-nitrophenyl β-hydroxy- and β-bromo-ethyl sulphides by Waldron and Reid (*J. Amer. Chem. Soc.*, 1923, **45**, 2399).

The results of a crystallographic examination of some of these compounds are summarised in the following table:

Substance.	*a* : *b* : *c*.	β.	Cleavage.
1 : 2$(NO_2)C_6H_4\cdot S\cdot C_2H_4\cdot OH$	0·5445 : 1 : 1·1416	—	(010)
1 : 2$(NO_2)C_6H_4\cdot S\cdot C_2H_4Cl$	0·9584 : 1 : 0·5126	—	(010)
1 : 2$(NO_2)C_6H_4\cdot S\cdot C_2H_4Br$	0·9590 : 1 : 0·5250	—	(010)
1 : 2$(NO_2)C_6H_4\cdot S\cdot C_2H_4I$	3·143 : 1 : 2·513	99° 16′	(010) & (100)
1 : 4$(NO_2)C_6H_4\cdot S\cdot C_2H_4Cl$	0·4752 : 1 : 0·4026	96° 54′	(100)
1 : 4$(NO_2)C_6H_4\cdot S\cdot C_2H_4Br$	1·8113 : 1 : 1·1187	96° 18′	—
1 : 4$(NO_2)C_6H_4\cdot S\cdot C_2H_4I$	0·5081 : 1 : 0·5160	104° 45′	—

EXPERIMENTAL.

Action of Sodium and Potassium Salts of Monothioethylene Glycol on o- *and* p-*Chloro- and Bromo-nitrobenzenes.*—The *o*-nitrophenyl thioether was first isolated from the products of the interaction of *o*-nitrochlorobenzene and monothioethylene glycol. o-*Nitrophenyl β-hydroxyethyl sulphide* was thus obtained in deep yellow, orthorhombic tables, m. p. 100° (Found: C, 48·2; H, 4·5; N, 7·1. $C_8H_9O_3NS$ requires C, 48·2; H, 4·5; N, 7·05%).

A better yield and a purer product were obtained by gradually heating *o*-nitrobromobenzene in spirit with monothioethylene glycol and potassium hydroxide, but the most convenient method

of preparation of this substance is through *o*-nitrothiophenol as described below.

When these preparations were repeated using *p*-chloronitrobenzene and *p*-bromonitrobenzene, reduction or some other subsidiary reaction was still more marked; the yellow product isolated, being practically indifferent to phosphorus pentachloride, was not *p*-nitrophenyl β-hydroxyethyl sulphide.

Preparation of the p-*Nitrophenyl Thioether of Monothioethylene Glycol.*—The *p*-compound was first isolated by a reaction analogous to that noted by Stadler (*loc. cit.*). The product was an oil, but it solidified after 3 weeks. It was dried on porous earthenware and recrystallised from dilute alcohol, and was identical with the material obtained more conveniently by the following method: *p*-Nitrochlorobenzene (31·5 g.) was covered with alcohol, a warm solution of sodium sulphide (48 g. of $Na_2S,9H_2O$) in dilute alcohol (60 c.c., 1 : 1) was added, and the mixture heated on the steam-bath until a vigorous reaction occurred. When this reaction had subsided, the mixture was heated for a further 5 minutes. Prolonged heating at this stage causes a decrease in the yield owing to oxidation of the thiophenol to disulphide (compare Willgerodt, *Ber.*, 1885, **18**, 331). The mixture was then poured into about 500 c.c. of water and cooled in a coal-gas atmosphere until the precipitated unchanged *p*-nitrochlorobenzene had solidified, and the liquid was rapidly filtered into an excess of sulphurous acid to precipitate the thiophenol and prevent oxidation. The thiophenol was quickly filtered off, dissolved in alcohol (30 c.c.), and added to a solution of potassium hydroxide (6 g. in 40 c.c. of water). The mixture was heated under reflux on the steam-bath with ethylene chlorohydrin (15 c.c.) until the dark colour faded, and the alcohol and volatile impurities were then removed in steam. The product (18 g.), which solidified on cooling, was *p*-nitrophenyl β-hydroxyethyl sulphide, which crystallised well from ether or carbon disulphide–petroleum as a pale yellow, finely crystalline solid, m. p. 62° (Found: C, 48·0; H, 4·6; N, 7·25. Calc.: C, 48·2; H, 4·5; N, 7·05%). Waldron and Reid (*loc. cit.*) give m. p. 59°.

Convenient Method of Preparation of the o-*Nitrophenyl Thioether.*—The analogous method can be shortened satisfactorily for the preparation of *o*-nitrophenyl β-hydroxyethyl sulphide. *o*-Nitrochlorobenzene and sodium sulphide are heated as described above and the product is poured into water. The precipitated nitrochlorobenzene, which does not solidify readily, is extracted with benzene, and the remaining solution is heated with the requisite amount of ethylene chlorohydrin for 15 minutes. It is not advisable to heat for longer than this, owing to the possible reduction of the

nitro-group by the sodium sulphide present in the solution. The yield is 17 g.

Preparation of m-*Nitrophenyl* β-*Hydroxyethyl Sulphide.*—An attempt to prepare this compound by the Stadler diazo-reaction (*loc. cit.*) gave an oil which did not crystallise. The *m*-nitrophenyl thioether was therefore made from *m*-nitrothiophenol, prepared as described by Leuckart (*J. pr. Chem.*, 1890, **41**, 179). The awkward diazotisation at great dilution was avoided thus: *m*-Nitroaniline (50 g.), dissolved in 150 c.c. of concentrated hydrochloric acid and 750 c.c. of water and cooled to 10°, was diazotised by adding sodium nitrite (26·5 g. in a little water) all at once, the temperature not being allowed to rise above 15°. This mixture was kept in ice for about 30 minutes, and the liquid was then filtered into a solution of potassium xanthate (75 g.) and borax (150 g.) in water (750 c.c.) at 70—75°. (It is necessary to add the diazo-solution cautiously, otherwise an explosive evolution of gas may be caused.) The mixture was finally heated until effervescence ceased. After cooling, the precipitated oil was removed in ether, the ether evaporated, and the crude xanthogenic ester hydrolysed. The dinitrodiphenyl disulphide, obtained by adding potassium ferricyanide to the resulting solution, was purified by recrystallisation and reduced with glucose and alkali (compare Lecher and Simon, *Ber.*, 1922, **55**, 2427), and the resulting thiophenol was converted into *m*-nitrophenyl β-hydroxyethyl sulphide in the same way as the *o*- and *p*-isomerides. The crude product was a dark oil which did not solidify. As the compound could not be distilled, even at pressures of 1 mm., it was heated at 150° with the equivalent of *p*-nitrobenzoyl chloride. The product solidified and, after recrystallising from toluene, m-*nitrophenyl* β-(p-*nitrobenzoyl*)*oxyethyl sulphide* was obtained as a pale yellow solid, m. p. 86° (Found: N, 8·25. $C_{15}H_{12}O_6N_2S$ requires N, 8·05%). This nitrobenzoyl derivative was hydrolysed by boiling alcoholic sodium hydroxide, the mixture poured into water, the oil which separated removed in ether, the extract dried, and the ether evaporated. The remaining oil solidified on being cooled in a freezing mixture, and m-*nitrophenyl* β-*hydroxyethyl sulphide* was obtained in pale yellow needles, m. p. 42·5°, by crystallisation from light petroleum (b. p. 40—60°) or warm water (Found: C, 48·0; H, 4·7; N, 7·0. $C_8H_9O_3NS$ requires C, 48·2; H, 4·6; N, 7·0%).

Little difficulty was encountered in getting the *mm'*-dinitrodiphenyl disulphide into a solid workable condition during the winter months, but when the preparation was repeated in warmer weather the disulphide solidified so slowly that it could not easily be obtained pure in quantity. The preparation of the *m*-compound has there-

fore been carried out without the isolation of the disulphide, as follows: The xanthogenic ester (20 g.) was hydrolysed with an alcoholic solution of sodium hydroxide (5 g. of sodium, 50 c.c. of alcohol, and 10 c.c. of water), and the reaction liquor was poured into water and extracted with carbon tetrachloride. The remaining solution was filtered, the filtrate dropping into water saturated with sulphur dioxide, and the precipitated thiophenol was removed in ether. The filtered ethereal solution was extracted with a solution of potassium hydroxide (10 g.) in two portions, and the extract heated on the steam-bath with ethylene chlorohydrin (10 c.c.) until the solution became clear. The precipitated oil, after being steam-blown, solidified when cooled and nucleated (yield, 9 g. of dry crude product).

Preparation of p-*Nitrobenzyl* β-*Hydroxyethyl Sulphide.*—*p*-Nitrobenzyl thiocyanate (m. p. 84°; compare Henry, *Ber.*, 1869, **2**, 638) was converted into *p*-nitrobenzyl thiocarbamate by Meyer's method ("Analyse und Konstitutions Ermittlung Organischen Verbindungen," 3rd Ed., p. 678), but it was subsequently found more convenient to use the method described by Gabriel and others (*Ber.*, 1895, **28**, 1027; 1896, **29**, 160: compare also Poggi, *Atti R. Accad. Lincei*, 1925, **2**, 423). A solution of the thiocyanate (50 g.) in concentrated sulphuric acid (250 c.c.) was kept in the ice-chest for 10 hours and then poured on ice. The precipitated thiocarbamate was filtered off and purified (m. p. 146°). The thiocarbamate was hydrolysed by boiling it under reflux with hydrochloric acid (10 parts of 20% acid) for 2 hours (compare Gabriel and Stelzner, *Ber.*, 1896, **29**, 160). On cooling, the oil, *p*-nitrobenzyl mercaptan, solidified.

The alternative method of preparation of *p*-nitrobenzyl mercaptan described by Price and Twiss (J., 1909, **95**, 1725) was found to be less satisfactory than the description would lead one to expect and certainly gave a product inferior both in yield and in purity to that obtained by the method described above.

The conditions for the condensation of the sodium salt of *p*-nitrobenzyl mercaptan and ethylene chlorohydrin are important, in that too great a concentration of alkali and heating to too high a temperature must be avoided, or else subsidiary reactions occur. The method used was as follows: To the mercaptan prepared from the thiocarbamate (12 g.) as described above, a solution of sodium hydroxide (3 g. in 60 c.c. of water) and ethylene chlorohydrin (7 c.c.) were added and the mixture was heated, in a flask provided with a stirrer, to 50° (thermometer dipping into the reaction liquid). The mixture was kept at this temperature for 15 minutes, during which an oil separated. 2*N*-Sodium hydroxide (10 c.c.) and ethylene chlorohydrin (3 c.c.) were then added and the mixture was heated

for a further 10 minutes. The reaction liquid was steam-blown to remove volatile impurities and cooled, the oil removed in ether, the extract dried, and the ether evaporated. After being kept for several days in a desiccator, the oil solidified (9 g.).

p-*Nitrobenzyl* β-*hydroxyethyl sulphide*, which is soluble in alcohol, ether, and benzene and slightly soluble in water, crystallises best from a mixture of equal volumes of carbon disulphide and light petroleum (b. p. 40—60°) in almost colourless needles, m. p. 37·5° (Found: C, 50·6; H, 5·4; N, 6·5. $C_9H_{11}O_3NS$ requires C, 50·7; H, 5·2; N, 6·6%).

In subsequent preparations, this compound was obtained as a solid by inoculating the steam-blown reaction liquor.

Preparation of p-*Nitrophenyl* γ-*Hydroxypropyl Sulphide.*—This compound was prepared by a method analogous to that used for the *p*-nitrophenyl β-hydroxyethyl sulphide and was isolated as an oil which solidified after a few days. It was recrystallised from carbon disulphide–light petroleum and obtained in pale yellow needles, m. p. 41·5°, which are slightly soluble in water and easily soluble in ether, alcohol, benzene, and acetone (Found: C, 50·5; H, 5·5; N, 6·6. $C_9H_{11}O_3NS$ requires C, 50·7; H, 5·2; N, 6·6%).

Preparation of Halogen Derivatives.

I. *Chloro-compounds.*—The *o*- and *p*-nitrophenyl β-chloroethyl sulphides were prepared by the action of phosphorus pentachloride on the hydroxy-compound (yield, 75%).

When this method was used for the preparation of *p*-nitrophenyl γ-chloropropyl sulphide, the yield was poor (45%), owing to a large amount of phosphoric ester being formed as a by-product. The preparation of this compound was therefore repeated using the Darzens reaction (*Compt. rend.*, 1911, **152**, 1314). The hydroxy-compound was dissolved in dimethylaniline (1·5 mols.), and thionyl chloride (1·5 mols.) gradually added, the mixture being kept cool. After 15 minutes, the mixture was heated on the steam-bath for 15 minutes and poured into dilute hydrochloric acid. The chloro-compound separated, and solidified on being cooled and scratched (yield, 87%). It was subsequently found that this method was preferable to the phosphorus pentachloride reaction for the preparation of the β-chloroethyl sulphides, in that the reaction product was much cleaner and solidified more readily (yield, 80—85%).

These ω-chloroalkyl sulphides are soluble in alcohol, acetone, benzene, and glacial acetic acid, and are best recrystallised from light petroleum or methyl alcohol.

Preparation of the Sulphoxides of the Halogenated Sulphides.—After the halogenated sulphide had been boiled for 15 minutes

with concentrated nitric acid (*d* 1·40), the product obtained on neutralising the solution had, even after several recrystallisations, an indefinite melting point.

The sulphide was dissolved in a little glacial acetic acid, and bromine (a slight excess above 1 mol.) added to the warm solution. As a dibromide (R·SBr_2·R′) did not crystallise, the solution was neutralised and a slight excess of aqueous sodium hydroxide added. The product in this case also had a diffuse melting point.

By adding a slight excess of hydrogen peroxide (30%) to a glacial acetic acid solution of the sulphide and keeping the mixture for 24 hours, compounds of sharp melting points were obtained. The sulphoxides crystallise well from either light petroleum or dilute acetic acid.

When oxidation of the iodoethyl sulphides was attempted with hydrogen peroxide, iodine was liberated and the pure sulphoxide was not isolated.

o-Nitrophenyl β-chloroethyl sulphide crystallises in deep yellow, orthorhombic needles, m. p. 51° (Found: C, 44·0; H, 3·8; Cl, 16·3. Calc.: C, 44·1; H, 3·7; Cl, 16·3%). The *sulphoxide* forms pale yellow needles, m. p. 84° (Found: N, 6·0. $C_8H_8O_3NClS$ requires N, 6·0%).

p-*Nitrophenyl* β-*chloroethyl sulphide* crystallises in pale yellow, monoclinic needles, m. p. 62° (Found: Cl, 16·3, 16·2. $C_8H_8O_2NClS$ requires Cl, 16·3%). The *sulphoxide* crystallises in colourless needles, m. p. 80° (Found: C, 41·2; H, 3·6; N, 6·0. $C_8H_8O_3NClS$ requires C, 41·1; H, 3·4; N, 6·0%).

m-*Nitrophenyl* β-*chloroethyl sulphide* forms pale yellow needles, m. p. 31° (Found: Cl, 16·2%).

p-*Nitrophenyl* γ-*chloropropyl sulphide* forms pale yellow needles, m. p. 50° (Found: N, 6·1; Cl, 15·4. $C_9H_{10}O_2NClS$ requires N, 6·1; Cl, 15·4%).

p-*Nitrobenzyl* β-*chloroethyl sulphide* forms almost colourless needles, m. p. 46—47° (Found: N, 6·1; Cl, 15·2. $C_9H_{10}O_2NClS$ requires N, 6·1; Cl, 15·4%).

H. *Bromo-compounds.*—These compounds were prepared by the action of phosphorus pentabromide on the hydroxy-compounds (see corresponding preparation of the chloro-compounds; p. 1671.) They are soluble in alcohol, benzene, acetone, and ether, and are best recrystallised from light petroleum.

o-*Nitrophenyl* β-*bromoethyl sulphide* crystallises in deep yellow, orthorhombic needles, m. p. 63° (Found: Br, 30·3. $C_8H_8O_2NBrS$ requires Br, 30·45%), and the *sulphoxide* in pale yellow needles, m. p. 112° (Found: N, 5·0%).

p-Nitrophenyl β-bromoethyl sulphide forms pale yellow, mono-

clinic needles, m. p. 59° (Found: Br, 30·1. Calc.: Br, 30·45%). Waldron and Reid (*loc. cit.*), who prepared this compound by the action of hydrobromic acid on the hydroxy-compound, give the melting point as 58°. The *sulphoxide* forms colourless needles, m. p. 100° (Found: Br, 28·6. $C_8H_8O_3NBrS$ requires N, 5·0; Br, 28·7%).

m-*Nitrophenyl* β-*bromoethyl sulphide* forms almost colourless, orthorhombic plates, m. p. 32° (Found: Br, 30·3%).

III. *Iodo-compounds.*—The interaction of phosphorus tri-iodide or phosphorus and iodine with the hydroxy-sulphides causes reduction and not simple replacement of the hydroxyl group. o- and p-*Nitrophenyl* β-*iodoethyl sulphides* have been obtained by heating the bromo-compound with a slight excess of sodium iodide in acetone solution for about 8 hours. They crystallise well from either methyl alcohol or light petroleum. The former crystallises in deep yellow plates, m. p. 64° (Found: I, 40·8. $C_8H_8O_2NIS$ requires I, 41·0%), and the latter in pale yellow plates, m. p. 67° (Found: I, 40·8%).

m-Nitrophenyl β-iodoethyl sulphide was obtained in a similar manner as a dark brown oil which did not crystallise and was not analysed. After it had been kept for a long time in the expectation of its solidifying, it was found in fact to be depositing crystals. These, on recrystallisation from petroleum (b. p. 90—120°), gave pale yellow plates, m. p. 136°, which contained sulphur and nitrogen but no iodine (Found: N, 8·2%; *M*, cryoscopic in molten camphor, 393). Sufficient of this substance was not obtained for a more detailed examination, but it seems probable that it was *di*-m-*nitrodiphenylthiol*cyclo*butane*, $\begin{matrix} NO_2\cdot C_6H_4\cdot S\text{—}CH\text{—}CH_2 \\ \qquad\qquad\quad\ \ \vert \qquad\ \vert \\ \qquad\qquad\quad CH_2\text{—}CH\cdot S\cdot C_6H_4\cdot NO_2 \end{matrix}$, which requires N, 7·7%; *M*, 362.

Crystallographic Measurements.

o-*Nitrophenyl* β-*hydroxyethyl sulphide* crystallises from acetone in deep yellow, orthorhombic crystals with $a : b : c = 0{\cdot}5445 : 1 : 1{\cdot}1416$. The forms observed are *b*(010), *c*(001), *r*(101) and *q*(011), the habit being tabular with *c* large (Fig. 1). The mean angular values obtained by measurement of seven crystals on a single-circle goniometer are: *cq**48° 47′, *cr**64° 30′, *rq* 73° 37′ (calc. 73° 31′), *bc* 89° 59′. There is a perfect cleavage in the plane (010). $d_4^{15°}$ (vac.) 1·472. The substance has strong positive double refraction. The plane of the optic axes is (100), the acute bisectrix emerging perpendicular to (010), and there is large dispersion of the axes.

o-*Nitrophenyl* β-*chloroethyl sulphide* was obtained in suitable crystals, after many trials, by slow crystallisation from cold ethyl

alcohol or from ethylene dichloride–ethylene chlorohydrin, in orthorhombic crystals with $a : b : c = 0{\cdot}9584 : 1 : 0{\cdot}5126$. The following are the forms observed and the respective mean angular values from eight crystals:

	a (100).	m (110).	x (21$\bar{2}$).	y (232).
ϕ	0° 0′	*43° 47′	*24° 47′	57° 54′
ρ	90° 0′	90° 0′	*29° 27′	43° 2′

The crystals are uniterminal and of prismatic habit similar to that shown in Fig. 2. $d^{18°}$, 1·480.

There is an excellent cleavage in the plane (010). Examination of cleavage planes in convergent polarised light shows that the substance has strong crossed axial dispersion. The optic picture is apparently uniaxial for the D line of sodium: red light (lithium flame) gives a biaxial picture with the axes well separated in the

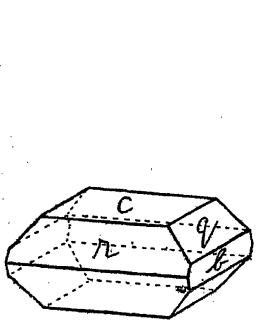


Fig. 1.

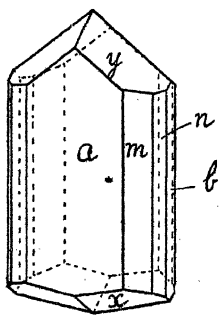


Fig. 2.

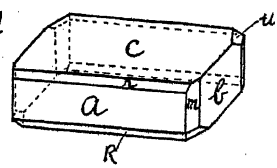


Fig. 3.

plane (100), whilst for green light (thallium) they are in the plane (001), the acute bisectrix remaining normal to (010) throughout.

o-*Nitrophenyl* β-*bromoethyl sulphide* separates from acetone in prisms (Fig. 2) belonging to the hemimorphic class of the orthorhombic system isomorphous with the foregoing, having $a : b : c = 0{\cdot}9590 : 1 : 0{\cdot}5250$. The following are the mean angular values (from six crystals):

	a (100).	m (110).	n (120).	b (010).	x (21$\bar{2}$).	y (232).
ϕ	0° 0′	*43° 48′	62° 25′	90° 0′	*23° 53′	56° 57′
ρ	90° 0′	90° 0′	90° 0′	90° 0′	*29° 52′	43° 10′

There is an excellent cleavage in the plane (010). $d^{17°}$ 1·742. A straight extinction was observed on (100). The acute bisectrix emerges perpendicular to (010), the axes being widely separated in the plane (001). The dispersion is large.

o-*Nitrophenyl* β-*iodoethyl sulphide* separates from acetone in large, deep yellow, monoclinic crystals (Fig. 3) with $a : b : c =$

3·143 : 1 : 2·513; β = 99° 16′. The following are the mean angular values (four crystals):

	a (100).	*m* (110).	*b* (010).	*r* (101).	*c* (001).	*R* (1̄01).	*u* (1̄12).
φ.....	0° 0′	*72° 8′	90° 0′	0° 0′	0° 0′	180° 0′	100° 32′
ρ.....	90° 0′	90° 0′	90° 0′	*44° 13′	9° 16′	33° 45′	47° 53′

There is a marked tendency for *b* to be replaced by a pair of vicinal faces. There are poor cleavages in the planes (010) and (100). $d^{16°}$ 2·026. The position of the optic axes could not be observed.

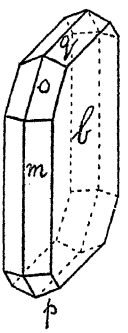


FIG. 4.

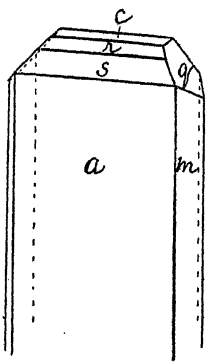


FIG. 5.

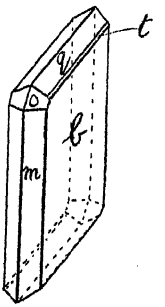


FIG. 6.

p-*Nitrophenyl* β-*chloroethyl sulphide* crystallises in the monoclinic system with *a* : *b* : *c* = 0·4752 : 1 : 0·4026; β = 96° 54′. The following are the mean angular values (4 crystals), the habit being as in Fig. 4.

	b (010).	*m* (110).	*q* (011).	*o* (111).	*p* (11
φ	0° 0′	*64° 45′	*16° 43′	67° 52′	298° 39′
ρ	90° 0′	90° 0′	*22° 48′	47° 15′	40° 28′

There is a poor cleavage in the plane (100). $d^{18°}$ 1·486. The extinction appears to be straight on (010). The position of the optic axes was not observed.

p-*Nitrophenyl* β-*bromoethyl sulphide* crystallises in the monoclinic system with *a* : *b* : *c* = 1·8113 : 1 : 1·1187; β = 96° 18′, the habit being as in Fig. 5. The following are the mean angular values (4 crystals):

	a (100).	*c* (001).	*m* (110).	*q* (011).	*s* (201).	*r* (101).
φ	0° 0′	0° 0′	*60° 57′	84° 54′	0° 0′	0° 0′
ρ	90° 0′	*6° 18′	90° 0′	*48° 18′	36° 19′	53° 45′

No marked cleavage was found. $d^{16°}$ 1·742. The extinction was straight on (100), but the position of the optic axes was not observed.

p-*Nitrophenyl* β-*iodoethyl sulphide* crystallises in the monoclinic system with *a* : *b* : *c* = 0·5081 : 1 : 0·5160; β = 104° 45′, the habit

being as in Fig. 6. The following are the mean angular values (3 perfect crystals):

	b (010).	*i* (021).	*q* (011).	*m* (110).	*o* (111).
ϕ	0° 0′	45° 11′	*63° 29′	*27° 24′	68° 21′
ρ	90° 0′	90° 0′	90° 0′	*29° 47′	54° 5′

There is no marked cleavage. $d^{17°}$ 1·938. The extinction on *b* is oblique at 17° 20′ to the edge *bm*. The optic axial plane coincides with (010), one optic axis being seen in the centre of the field when the observation is normal to the plane (100). The dispersion is extremely high.

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CCXIV.—*The Influence of the Sulphur Atom on the Reactivity of Adjacent Atoms or Groups. Part II. Comparative Reactivities of Chlorine in some β- and γ-Chloro-sulphides.*

By GEORGE MACDONALD BENNETT and WILLIAM AMBLER BERRY.

IN Part I of this series (this vol., p. 477), a qualitative comparison was made of the reactivities of the chlorine atoms in the β-, γ-, and δ-positions relative to a sulphur atom. In the present communication, we describe quantitative measurements of the reactivities of the chlorine atoms in some β- and γ-chloro-sulphides, namely, in the *o*-, *m*-, and *p*-nitrophenyl β-chloroethyl sulphides, *p*-nitrobenzyl β-chloroethyl sulphide, and *p*-nitrophenyl γ-chloropropyl sulphide, described in the preceding paper, together with the unsubstituted phenyl β-chloroethyl- and γ-chloropropyl-sulphides.

Comparative measurements were first made of the extent of their interaction with aqueous alcoholic sodium hydroxide solution during a short interval of time at 55°. With respect to this test, the substances arrange themselves in order of diminishing reactivity as follows: *o*- and *p*-nitrophenyl β-chloroethyl sulphide>*m*-isomeride≫phenyl β-chloroethyl sulphide>phenyl γ-chloropropyl sulphide and its *p*-nitro-derivative.

The nitrobenzyl sulphide suffered some profound decomposition in presence of alkali, doubtless owing to the activation of the methylene group situated between the sulphur atom and the nucleus. No attempt was made to calculate a velocity coefficient for this reaction, since from analogy with the behaviour of other chloro-sulphides (compare Bales and Nickelson, J., 1922, **121**, 2137) it is probable that two reactions are involved, namely, a true hydrolysis

to the corresponding hydroxy-compound and the formation of an unsaturated sulphide by removal of one molecular proportion of hydrogen chloride. The result does, however, show that, in agreement with the conclusions previously reached concerning β- and γ-chloro-sulphides (Bennett and Hock, J., 1925, **127**, 2671; this vol., p. 477), the γ-chloropropyl sulphide is in each case less reactive than the closely related β-chloroethyl compound.

In order to obtain a more accurate comparison of the reactivities of these substances we examined their hydrolysis by 50% aqueous alcohol at 75°, a reaction similar to that used by Olivier for a similar purpose (*Rec. trav. chim.*, 1922, **41**, 646) and likely to be free from the defect of subsidiary reactions. We have therefore made a comparison of the initial velocities of hydrolysis; the results are in column 4 of Table I.

The reaction of the chloro-sulphides with piperidine was also examined with a view to quantitative measurement, but it was discarded when the product of the reaction was found to be a mixture. Finally, we also examined the reaction of these substances with potassium iodide, since this had been found to be quantitative and free from subsidiary reactions in the preparation of the β-iodo-sulphides (see preceding paper). Similar reactions have, moreover, been studied by Conant and his colleagues (Conant, Kirner, and Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 488) and found suitable for accurate measurement. The velocities of reaction of these chloro-sulphides have been measured in acetone solution at 55°. The method of determining ionic iodine described by these authors was found to be unsuitable and a modified procedure was worked out. The reaction was in all cases bimolecular and the coefficients are given in Table I.

TABLE I.

	Reaction with potassium iodide at 55°.		Hydrolysis at 75°.
Substance.	k.	Relative values.	Relative values.
$Ph{\cdot}S{\cdot}C_2H_4Cl$	0·091	1·00	1·00
$o\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·180	1·98	0·023
$m\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·189	2·09	0·083
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·257	2·62	0·052
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C_2H_4Cl$	0·215	2·36	—
$Ph{\cdot}S{\cdot}C_3H_6Cl$	0·330	3·52	0·0031
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_3H_6Cl$	0·836	9·19	0·0010

Interpretation of the Results.

The substances are arranged with respect to the hydrolysis in an order which is the opposite of that shown in the reaction with potassium iodide. This contrast must depend on the nature and

mechanism of the two reactions used. It may be explained if the reactions involved are of opposite polar type. A similar contradiction was pointed out by Conant, Kirner, and Hussey (*loc. cit.*), who remark with reference to certain chloro-compounds that the increased reactivity with potassium iodide " appears to be just the reverse of what would be predicted from a consideration of polarity." A consideration of the influence of certain activating groups "would," they point out, " lead to the conclusion that the chlorine atom of $Ph{\cdot}CO{\cdot}CH_2Cl$ was more *positive* than the chlorine atom of benzyl chloride: yet it is 500 times more reactive in a reaction in which the chlorine is *eliminated as a negative ion* and is *replaced by a negative ion*. . . . It seems evident that no adequate interpretation of the facts can be stated solely in terms of polarity." This difficulty is in reality the same as that presented by our own opposed sets of reaction velocities. A further clear case of the same kind is shown in Table II, which gives the results of the comparison of benzyl chloride and its nitro-compounds as determined by hydrolysis (Olivier, *loc. cit.*) and by the potassium iodide reaction (Conant and others).

TABLE II.

Substance.	Relative reactivity with KI at 50°.	Relative reactivity with water at 30°.
$Ph{\cdot}CH_2Cl$	1	1
o-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$	9·15	0·047
m-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$	3·96	0·057
p-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$	6·95	0·044

All these anomalies disappear if it be admitted that, whilst a negative charge on the chlorine atom accelerates the hydrolysis (compare Oxford and Robinson, J., 1926, 384), it is a positive charge on the chlorine atom that makes it react more rapidly with potassium iodide. This will be the case if, as we suggest, the latter reaction involves two stages, the first of which is the formation of a complex between the organic chloro-compound and the iodide ion. In the second stage, the neutral organic iodo-compound is formed by the ejection of a chlorine ion from the complex. The first stage of the reaction will proceed at a higher velocity the greater the *positive* charge on the chlorine atom, since this will favour combination with the negative iodine ion. On this assumption, our two sets of data become consistent among themselves, and with the electron distribution deduced for β- and γ-chloro-sulphides in Part I of the series. The reaction velocities observed for $Ph{\cdot}S{\cdot}C_2H_4Cl$ and $Ph{\cdot}S{\cdot}C_3H_6Cl$ lie respectively below and above that found by Conant and his colleagues for $Ph(CH_2)_4Cl$, namely, 0·211.* This confirms

* This value has been obtained from their figure by use of their interpolation formula and multiplication by 2·302.

the suggestion made in Part I that actually the chlorine atom in the β-position is negatively, and in the γ-position positively, charged as compared with the normal.

Kirner (*J. Amer. Chem. Soc.*, 1926, **48**, 2745) has recently found three ethers to have reactivities in the order $PhO{\cdot}C_2H_4Cl < PhO{\cdot}C_3H_6Cl > PhO{\cdot}C_4H_8Cl$, with respect to the potassium iodide reaction. The influence of an atom of oxygen and one of sulphur in a molecule should be similar, if similarly situated, so that this result is in qualitative agreement with the conclusion arrived at in Part I that chlorine varies in reactivity (to hydrolysis) with position relative to sulphur in the order : $\beta > \gamma < \delta$.

The introduction of a nitro-group into the nucleus of any of these compounds—chloro-sulphides or benzyl chlorides—gives a positive charge to the chlorine atom and so alters the velocities of the two reactions discussed in the directions observed. No large difference of effect was found with orientation of the nitro-group in the *o*-, *m*-, and *p*-positions in the sulphides, which is consistent with the conclusion of Oxford and Robinson (*loc. cit.*) that " the alternating effect of a nitro-group cannot be discerned beyond the limits of the conjugated system of which it forms a part." In the case of the reaction with aqueous alcoholic sodium hydroxide, the introduction of the nitro-group actually increases the reactivity in the β-chloro-sulphides. Since in the true hydrolysis the converse effect is observed, the increase must be due to the subsidiary reaction involving the elimination of hydrogen chloride.

Experimental.

Preparation of β-Hydroxyethyl and γ-Hydroxypropyl Phenyl Sulphides.—These compounds were obtained by the condensation of sodium thiophenoxide and the respective chlorohydrins : The thiophenol (15 g.), a solution of sodium hydroxide (6 g. in 100 c.c. of water), and ethylene chlorohydrin (12 c.c., or 15 c.c. of trimethylene chlorohydrin in the case of the propyl compound) were mixed and heated to about 60°. When the solution had become neutral to litmus, 20 c.c. of *N*-sodium hydroxide and 4 c.c. of the chlorohydrin were added and the mixture was heated for a further 15 minutes. The precipitated oil was removed in ether.

An attempt to distil phenyl β-hydroxyethyl sulphide under diminished pressure gave an unsaturated compound, probably due to the splitting out of water from the side chain giving rise to phenyl vinyl sulphide. The preparation of the chloroethyl sulphide was therefore carried out with the crude hydroxy-compound by means of the Darzens reaction (preceding paper, p. 1671). The products were removed by ether extraction.

Phenyl β-chloroethyl sulphide is a colourless liquid with a rather pungent smell and a very slight vesicant action; b. p. 117°/12 mm. (Found: Cl, 20·4. Calc.: Cl, 20·55%). *Phenyl γ-chloropropyl sulphide* is a colourless liquid and is not appreciably vesicant; b. p. 137°/13 mm. (Found: Cl, 18·8. $C_9H_{11}ClS$ requires Cl, 19·0%).

Reaction of the Chloro-sulphides with Piperidine.—This reaction was investigated with a view to employ it as a means of determining the relative reactivities of the chloro-compounds.

o-Nitrophenyl β-chloroethyl sulphide (1 g.) was boiled under reflux for 8 hours with piperidine (1·2 g.) and alcohol (10 c.c.). The mixture was then made slightly alkaline and distilled in steam to remove the alcohol and excess of piperidine. The remaining oil was dissolved in ether, and the solution dried. On passing dry hydrogen chloride into the ethereal solution, a precipitate was formed (0·7 g.), m. p. 231°. This compound was soluble in water and the addition of sodium hydroxide caused the precipitation of an oil, which solidified to give pale yellow crystals, m. p. 45°, of *o-nitrophenyl β-piperidinoethyl sulphide* (Found: N, 10·7. $C_{13}H_{18}O_2N_2S$ requires N, 10·5%). The compound precipitated from the ethereal solution was therefore the hydrochloride of this base.

Evaporation of the remaining ethereal solution gave a dark oil which did not crystallise. It gave a negative result with a test for chlorine, but its reaction with potassium permanganate as compared with that of the original chloro-sulphide indicated the presence of an unsaturated group. It was therefore probably *o*-nitrophenyl vinyl sulphide.

Further experiments with only one equivalent of piperidine did not give improved yields of the hydrochloride.

p-Nitrophenyl β-chloroethyl sulphide, when subjected to the same reaction, also gave similar products, namely, a base and an unsaturated compound. The hydrochloride had m. p. 217° and the free base, *p-nitrophenyl β-piperidinoethyl sulphide*, melted at 52°.

Reaction of the Chloro-sulphides with Alcoholic Sodium Hydroxide.—A comparison of the reactivities of the chloro-sulphides with alcoholic sodium hydroxide was made in the following way: The chloro-sulphide (0·001 mol.) was weighed into a test-tube, 5 c.c. of absolute alcohol were pipetted on to it, and the mixture was gently warmed to bring the organic matter into solution. *N*/5-Sodium hydroxide (5 c.c.) was added, and the tube was stoppered and immediately immersed in a thermostat. After a definite period of time, the contents of the tube were washed out and titrated with standard hydrochloric acid.

The following table summarises the results :

Compound.	Temp.	Time (hrs.).	Titration of reaction mixture (c.c. of 0·1*N*-HCl).	Amount of NaOH (expressed as c.c. of acid).
o-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$	55°	0·5	1·87	8·13
m-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$	55	0·5	2·87	7·13
p-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$	55	0·5	1·75	8·25
$Ph \cdot S \cdot C_2H_4Cl$	55	2·0	7·16	2·84
$Ph \cdot S \cdot C_3H_6Cl$	55	2·0	9·24	0·76
p-$NO_2 \cdot C_6H_4 \cdot S \cdot C_3H_6Cl$	55	2·0	9·22	0·78

Some experiments were also conducted at 42° :

p-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$	42°	0·5	4·00	6·00
$Ph \cdot S \cdot C_2H_4Cl$	,,	,,	9·55	0·45
p-$NO_2 \cdot C_6H_4 \cdot S \cdot C_3H_6Cl$	,,	,,	9·80	0·20
$Ph \cdot S \cdot C_3H_6Cl$	,,	,,	9·75	0·25

When *p*-nitrobenzyl β-chloroethyl sulphide was subjected to this reaction, some other reaction than replacement of chlorine by hydroxyl took place, for a brown compound was produced along with a peculiar odour which was always present when an attempt to condense the sodium salt of *p*-nitrobenzyl mercaptan with ethylene chlorohydrin did not give the desired thioether. The hydroxy-compound is also decomposed by sodium hydroxide in a manner similar to that of the chloro-compound.

It follows that with respect to the reaction with sodium hydroxide in alcoholic solution, these compounds may be arranged as follows in descending order of reactivity: *p*-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$ > *o*-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$ > *m*-$NO_2 \cdot C_6H_4 \cdot S \cdot C_2H_4Cl$ > $Ph \cdot S \cdot C_2H_4Cl$ > $Ph \cdot S \cdot C_3H_6Cl$ and *p*-$NO_2 \cdot C_6H_4 \cdot S \cdot C_3H_6Cl$. The method used is not sufficiently accurate to enable a statement to be made as to which of the last two compounds is the more reactive.

Hydrolysis of the Chloro-sulphides.—The chloro-sulphide (0·001 g.-mol.) was dissolved in alcohol (25 c.c.), and the solution placed in a thermostat at 75° for several minutes. Water (25 c.c.) which had been immersed in the thermostat was then added, the time noted, and the reaction flask stoppered. After a definite time interval, the contents of the flask were cooled, diluted with water, and titrated with standard sodium hydroxide solution.

From this titration value, the proportion of hydrolysis (x) was calculated, and values for the relative reactivities were obtained from the expression

$$\text{Relative reactivity} = t_1 \log \{1/(1 - x_2)\}/t_2 \log \{1/(1 - x_1)\},$$

t_1 and x_1 being the values found for $Ph \cdot S \cdot C_2H_4Cl$.

The following table summarises the results :—

Substance.	x.	Time (mins.).	Rel. reactivity.
$Ph{\cdot}S{\cdot}C_2H_4Cl$	0·748	15	1·0
$o\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·243	130	0·023
$m\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·628	130	0·083
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·460	130	0·052
$Ph{\cdot}S{\cdot}C_3H_6Cl$	0·081	300	0·003
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_3H_6Cl$	0·027	300	0·0010

This order of relative reactivities was confirmed in two further sets of experiments.

p-Nitrobenzyl β-chloroethyl sulphide is omitted from the above list, since the product of its hydrolysis was undoubtedly a mixture. After the hydrolysis of *p*-nitrophenyl β-chloroethyl sulphide, the corresponding hydroxy-compound crystallised from the reaction mixture. *p*-Nitrobenzyl β-chloroethyl sulphide, however, yielded an oily product which did not crystallise even on inoculation with a crystal of the pure hydroxy-compound. An unsaturated impurity was found to be present.

Reaction of the Chloro-sulphides with Potassium Iodide.—This reaction was applied under conditions similar to those used by Conant and others (*loc. cit.*), namely, the initial concentrations of the organic chloro-compound and the potassium iodide were in the ratio 5 : 1, the iodide concentration being approximately 0·04*N*. Absolute acetone, purified as described by Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 233), was used as solvent.

Andrews's method for estimation of iodide in presence of chloride (*J. Amer. Chem. Soc.*, 1903, **25**, 756), as used by Conant and others, was found to be unsatisfactory in the present investigation, owing to reaction between the iodic acid and the organic sulphide in the chloroform used for indicator. Even after removal of the organic compound, the end-point with chloroform as indicator was not well defined, and starch could not be used owing to the great acidity of the solution.

A convenient method in which starch can be used as indicator was found in that described by Lang (*Z. anorg. Chem.*, 1922, **122**, 332), depending on the addition of an oxidising agent (*e.g.*, potassium iodate) to an acid solution of an iodide in presence of hydrogen cyanide. The iodine is converted quantitatively into iodine cyanide, which does not colour starch. As the acidity of the solution is approximately normal (when hydrochloric acid is used), starch can be used as indicator. Acetone in the titration flask causes a temporary fading of the blue starch–iodide colour when near the end-point, *e.g.*, a further drop of iodate solution regenerates the blue colour, which then fades again on standing: this occurs until the true end-point is reached, after which addition of iodate no longer causes an evanescent blue colour. Thus, although the

acetone does not affect the value for the end-point, its presence makes the determination difficult. The acetone was therefore removed by passing a current of steam through the solution before titrating it.

The experimental procedure adopted in these measurements was as follows: 50 C.c. of 0·04*N*-potassium iodide (in the pure acetone) were added to 0·01 g.-mol. of the organic halide contained in a conical flask. The organic compound dissolved rapidly and as soon as it was thoroughly mixed, 5 c.c. of the mixture were pipetted into a separating funnel containing 20 c.c. of water. This precipitated the organic halide and prevented any reaction: in the estimation as subsequently described, this reading gave the blank for calculating the concentration of the potassium iodide in the reaction and also the value for A_0 in the formula (below). 5 C.c. lots of the mixture were pipetted into each of a series of nine tubes (made of stout glass tubing, about 6 in. long and 0·5 in. inside diameter) which were then sealed up in the blow-pipe flame. These tubes were placed in a thermostat at 55·0°.

After about 30 minutes, one of the tubes was removed and opened and the contents were washed into water (10 c.c.). The time was noted and this was counted as the zero time of the readings. The whole was then extracted with chloroform (four portions of 5 c.c.), the chloroform extracts being washed with water (10 c.c.) to recover any potassium iodide solution which may have been removed mechanically in the chloroform. This aqueous washing of the chloroform was finally extracted with 5 c.c. of chloroform. The aqueous solution was then distilled in steam for 3 minutes to remove the chloroform and acetone, a splash-bulb being used to prevent any loss. The mixture, which then had a bulk of about 70 c.c., was cooled and concentrated hydrochloric acid (15 c.c.) and potassium cyanide solution (8 c.c. of $N/2$) were added. It was titrated against 0·003*M*-potassium iodate solution, starch being used as indicator.

At definite time intervals, tubes were removed from the thermostat and worked up as indicated above. The velocity coefficient was calculated from the bimolecular formula

$$k = \frac{2{\cdot}302}{4b(t_2 - t_1)} \log_{10} \frac{(4A_0 + A_2)A_1}{(4A_0 + A_1)A_2},$$

where A_0 = blank titration value at the commencement of reaction, A_1 = titration value at time t_1, A_2 = titration value at time t_2, and b = the concentration of potassium iodide in the reaction (calc. from A_0), time being measured in hours and the concentrations in g.-mol. per litre.

Except in one instance, the greatest percentage variation among the values for k in a series of measurements is less than 10%, which

is satisfactory in view of the necessarily complicated experimental procedure.

o-*Nitrophenyl* β-*Chloroethyl Sulphide.*—0·01 G.-mol. mixed with 50 c.c. of 0·04*N*-potassium iodide in pure acetone. Temperature of thermostat 55·0°. The titrations (*A*) are expressed as c.c. of 0·003*M*-potassium iodate.

(t_2-t_1) in hrs.	*A*.	*k*.	(t_2-t_1) in hrs.	*A*.	*k*.
—	32·55 (A_0)	—	10	22·16	0·181
0	31·11 (A_1)	—	14	19·46	0·181
2	28·89	0·193	18	17·39	0·176
4	27·04	0·184	22	15·44	0·174
6	25·55	0·173	27	13·42	0·177
				Mean	0·180

Mean value in an independent experiment, 0·177.

The following table summarises the measurements of the reaction velocities of the remaining compounds studied.

In each case 0·01 g.-mol. of the chloro-sulphide was dissolved in 50 c.c. of 0·04*N*-potassium iodide solution, and the temperature of the reaction was 55·0°.

Substance.	Limits of *k*.	*k*.	*k* (independent observation).
m-$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·180—0·198	0·189	0·187
p-$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_2H_4Cl$	0·250—0·267	0·257	0·252
p-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C_2H_4Cl$ ...	0·206—0·227	0·215	0·235
p-$NO_2{\cdot}C_6H_4{\cdot}S{\cdot}C_3H_6Cl$	0·817—0·886	0·836	0·820
$Ph{\cdot}S{\cdot}C_2H_4Cl$	0·084—0·100	0·091	0·086
$Ph{\cdot}S{\cdot}C_3H_6Cl$	0·321—0·342	0·330	0·343

We wish to thank the Chemical Society for assistance in the purchase of materials, and the Department of Industrial and Scientific Research for a maintenance grant which has enabled one of us (W. A. B.) to take part in the work described in this and the preceding paper.

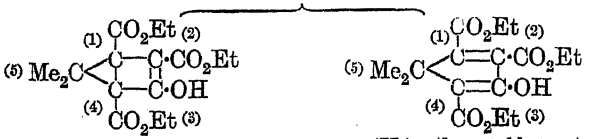
THE UNIVERSITY, SHEFFIELD. [*Received, April 8th*, 1927.]

CCXV.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part VIII. The Differing Effects of the* gem-*Dimethyl and* spirocyclo*Hexane Groupings on the Direction of Blocking of an Intra-annular Tautomeric System by Substitution.*

By CHRISTOPHER KELK INGOLD and ERNEST ARTHUR SEELEY.

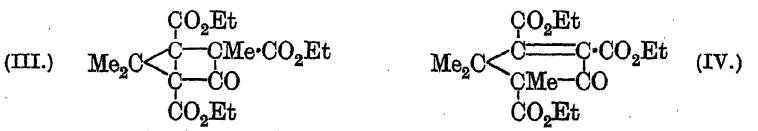
IN Parts I and II (Farmer and Ingold, J., 1920, **117**, 1362; Farmer, Ingold, and Thorpe, J., 1922, **121**, 128) proof was adduced that the bridged-ring ester (I), first prepared by Perkin and Thorpe (J.,

1901, **79**, 729), behaved as though it also had the structure (II), and that its derivatives and hydrolysis products exhibited similar evidence of tautomeric behaviour.



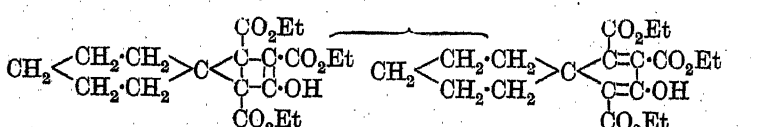
(I.) (*more stable type*) (II.) (*less stable type*)

It then became of interest to ascertain which of the two types of structure would be perpetuated when substitution converted the tautomeric parent into a static derivative. Thus the sodio-derivative of the above hydroxy-ester might methylate on carbon in position 2 through form (I) or in position 4 through form (II), giving, in the first case, a stable bridged ring, and, in the second, a stable monocyclic derivative. This question was answered in Part V (J., 1923, **123**, 3303) where it was shown that the static methyl derivative possessed the bridged constitution (III) and not the monocyclic structure (IV):



(*static*; *formed*)

Part IV (J., 1923, **123**, 853) recorded an investigation of the derivatives of a hydroxy-ester (V, VI) analogous to (I, II) but containing a *spirocyclo*hexane ring in place of the *gem*-dialkyl group. Ingold and Thorpe (J., 1919, **115**, 320) had adduced theoretical reasons for believing that the bridged structure in type (V) would be less stable than that in type (I); and it was subsequently found (Part IV, *loc. cit.*) that the reactions indicating the *cyclo*pentene phase are actually more pronounced, and those indicating the bridged phase less pronounced, in the *cyclo*hexane than in the *gem*-dimethyl series.

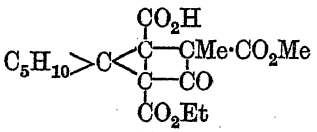


(V.) (*less stable form*) (VI.) (*more stable form*)

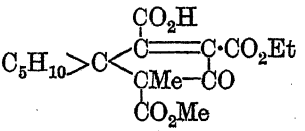
It therefore seemed possible that the blocking of the mobile intra-annular system by methylation might occur through the unbridged form in the *cyclo*hexane series, the methyl group entering

in position 4, in contrast to the established course of the reaction in the *gem*-dimethyl series.

When the methylation product obtained from the sodio-derivative of the *spirocyclo*hexane ester (V, VI) is boiled with hydrochloric acid, a solid acid ester is obtained which may be formulated either as (VII) or as (VIII) according as the methyl group occupies position 2 or 4.



(VII.)

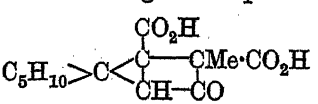


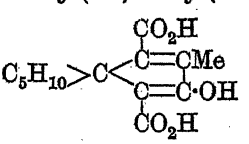
(VIII.) (*static*; *formed*)

These formulæ assume that one of the carbethoxyl groups has been converted into a carbomethoxyl group during methylation; a partial conversion of this nature was established by Ingold and Thorpe (*loc. cit.*) and similar interchanges have frequently been recorded. The position given to the free carboxyl group is tentatively assigned on the grounds that the acid ester does not evolve carbon dioxide at its melting point. Any doubt which might be entertained on these points does not affect the substance of this argument. Either type of formula necessarily represents the acid ester as a substance in which intra-annular tautomerism has been suspended by substitution.

Hydrolysis of the acid ester with alcoholic potassium hydroxide leads to the production of a dibasic acid, $C_{13}H_{16}O_5$, the properties of which determine the position of the methyl group. The possible constitutions of an acid of this composition derived from an acid ester having formula (VII) are given by formulæ (IX) and (X); on the other hand, if the acid ester possessed the structure (VIII), the dibasic acid might be represented either by (XI) or by (XII).

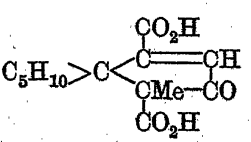
(IX.)

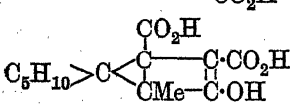




(X.)

(XI.)



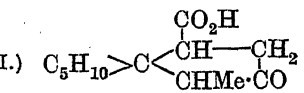


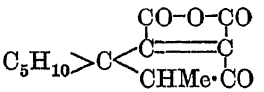
(XII.)

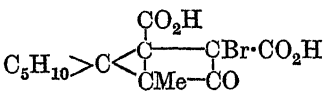
Of these four formulæ, (XII) alone is consistent with the following properties of the isolated acid: (*a*) It gives a deep violet colour with ferric chloride, and is therefore a β-hydroxyacrylic acid. (*b*) It readily yields a stable cyclic anhydride, from which the original acid can be recovered after fission of the anhydride ring

with hot alkali. (*c*) On treatment with a cold dilute solution of bromine in acetic acid, the dibasic acid undergoes nuclear substitution, one atom of hydrogen being replaced (compare Part IV, *loc. cit.*, pp. 857—862).

Formula (XII) connotes, of course, only one of the possible intra-annular tautomeric forms possessed by the dibasic acid $C_{13}H_{16}O_5$, and we regard formulæ (XIV) and (XV) as representing the most probable constitutions of its anhydride and bromo-derivative, respectively.

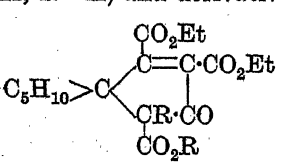
(XIII.) 

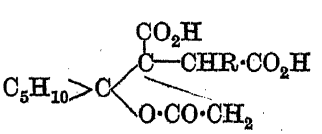

(XIV.)

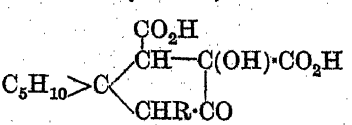

(XV.)

These observations show that the static methylation product (VIII) has a formula of the type assigned to it, the tautomerism of the *spirocyclo*hexane five-carbon nucleus having been suppressed by methylation in a direction conforming to the general chemical differences between this series and the corresponding *gem*-dimethyl series of intra-annular tautomeric compounds.

These experiments necessitate a revision of the structures which Ingold and Thorpe (*loc. cit.*) assigned to certain derivatives of the mobile ester (V, VI) before the intra-annular tautomerism of the five-carbon nucleus was discovered. Thus the ester was assumed to methylate in position 2 by analogy with the methylation of the *gem*-dimethyl ester (I, II). The formula now suggested for the methylated product is XVI (R=Me), the probable structures of the fission products, m. p.'s 172° and 185°, being represented by XVII and XVIII (R=Me). Corresponding changes are necessary in the structures of the homologues (XVI, R=Et; XVII, R=Et; XVIII, R=H) and derivatives:


(XVI.) {R = Me, oil. R = Et, oil.


(XVII.) {R = Me, m. p. 172°. R = Et, m. p. 149°.


(XVIII.) {R = Me, m. p. 185°. R = H, m. p. 206°.

EXPERIMENTAL.

Methyl Ethyl Hydrogen 4-*Methyl*-5-cyclo*hexane*spiro-Δ^1-cyclo*pentan*-3-*one*-1 : 2 : 4-*tricarboxylate* (VIII).—The yellow sodio-derivative (20 g.) of ethyl 5-*cyclo*hexane*spirodicyclo*penten-3-ol-1 : 2 : 4-tricarboxylate was heated with a large excess of methyl iodide as described by Ingold and Thorpe (*loc. cit.*), and the crude methylation product (19 g.) was boiled for 12 hours with 20% hydrochloric acid. On extraction with ether a stiff gum was obtained which solidified after 2 months; the *acid ester* was then crystallised from ether–ligroin. It separated in prisms, m. p. 92—93° (Found: C, 60·9, 61·0; H, 6·7, 6·8; *M*, by titration, 339. $C_{17}H_{22}O_7$ requires C, 60·4; H, 6·6%; *M*, monobasic, 338).

4-*Methyl*-5-cyclo*hexane*spiro-(0 : 1 : 2)-dicyclo*penten*-3-*ol*-1 : 2-*dicarboxylic Acid* [4-*Methyl*-5-cyclo*hexane*spiro-(0 : 1 : 2)-dicyclo*pentan*-3-*one*-1 : 2-*dicarboxylic Acid*] (XII).—The above acid ester was boiled with 2·2 parts of potassium hydroxide in 4*N*-solution in absolute methyl alcohol, and after 6 hours the precipitate was collected, dissolved in water, and decomposed by dilute hydrochloric acid (carbon dioxide was evolved). The aqueous solution was extracted thoroughly with ether, and the *acid* thus recovered was crystallised first from ether–ligroin and then from ether (Found: C, 61·8; H, 6·4; *M*, by titration, 126·3. $C_{13}H_{16}O_5$ requires C, 61·8; H, 6·4%; *M*, dibasic, 126·1).

The acid has m. p. 214—216°, and with an aqueous alcoholic solution of ferric chloride gives an intense violet coloration which after several minutes is replaced by a yellowish-brown precipitate. A dilute solution of permanganate was decolorised in about 1 minute. Oxidations with permanganate and with ferricyanide were tried on a larger scale under various conditions, but the products could not be crystallised.

The Anhydride (XIV).—The acid (0·4 g.) was heated for 20 minutes with 6 c.c. of acetyl chloride at 100°, and the residue obtained on evaporation was rubbed with aqueous sodium hydrogen carbonate and dried on porous porcelain. Subsequent treatment indicated the presence of a small amount of unchanged acid, which was difficult to remove by crystallisation, and the product was therefore again treated with acetyl chloride and the residue crystallised twice from ether–ligroin; large, pale green prisms, m. p. 95°, were then obtained (Found by microanalysis: C, 65·9, 66·3; H, 6·0, 6·6. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%). The green colour of this substance, which is absent from the acid, is similar to that of ketomalonic ester, which also contains a cross-conjugated system. The anhydride is affected only very slowly by boiling water, but is

hydrolysed by hot aqueous sodium hydroxide, yielding the sodium salt of the original acid, m. p. 214—216° (mixed m. p. the same). A solution of the anhydride in ether–ligroin gives precipitates with *p*-toluidine and *p*-chloroaniline which are soluble with effervescence in sodium hydrogen carbonate and are therefore presumably the substituted amic acids. The anhydride does not give a colour with ferric chloride, but rapidly decolorises permanganate.

The methyl-alcoholic filtrate from the potassium salt of the dibasic acid, on being worked up for organic acids, yielded a considerable amount of gum together with a small amount of a solid acid, which, after several crystallisations from benzene, had m. p. 102—105°, but still did not appear quite pure. The investigation of this had to be discontinued for lack of material.

2-*Bromo*-4-*methyl*-5-cyclo*hexane*spiro-(0 : 1 : 2)-dicyclo*pentan*-3-*one*-1 : 2-*dicarboxylic Acid* (XV).—The above dibasic acid (0·37 g.), dissolved in 10 c.c. of glacial acetic acid, was treated with 3 c.c. of a 10% solution of bromine in acetic acid (theory, 2·4 c.c.). After 4 hours, the bromine was nearly decolorised. On concentration of the acetic acid solution at the ordinary temperature, the *bromo-acid* readily crystallised. It separated from ether–benzene in small prisms, m. p. 197—198° (Found: Br, 23·6. $C_{13}H_{15}O_5Br$ requires Br, 24·1%).

4-*Methyl*-5-cyclo*hexane*spirocyclo*pentan*-3-*one*-1-*carboxylic Acid* (XIII).—The acid ester (VIII) was heated for 3 hours at 135—150° with constant-boiling hydriodic acid. The liquid was extracted with ether, and the iodine removed from the extract with aqueous sodium hydrogen sulphite. The product obtained on evaporation of the ether contained sulphur, but this was readily eliminated by crystallisation from ether–ligroin, which yielded the pure monobasic acid, m. p. 114—116° (Found: C, 68·4; H, 8·6. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%).

The *semicarbazone*, prepared from the acid, semicarbazide hydrochloride, and aqueous sodium acetate, has m. p. 223° (Found: C, 58·6; H, 8·2. $C_{13}H_{21}O_3N_3$ requires C, 58·8; H, 7·9%).

Gums which cannot be crystallised were obtained on attempting to oxidise this ketonic acid with permanganate and ferricyanide at 20—60°.

We desire to thank the Chemical Society for defraying part of the cost of this investigation.

THE UNIVERSITY, LEEDS. THE TECHNICAL COLLEGE, DERBY.

[*Received, May 11th,* 1927.]

CCXVI.—*The Nature of the Alternating Effect in Carbon Chains. Part XX. The Conditions underlying Vicinal Substitution in* o-*Substituted Benzenes containing* op-*Orienting Groups.*

By CHRISTOPHER KELK INGOLD and ERNEST WALTER SMITH.

IN Part V it was shown (Ingold and Ingold, J., 1926, 1310) that whilst acet-*o*-anisidine (I) and aceto-*N*-methyl-*o*-anisidine are nitrated mainly in the 4- and 5-positions, *ON*-diacetyl-*o*-aminophenol (II), in which the disparity between the *op*-orienting powers of the groups is much greater, yields a large proportion of a vicinal nitro-derivative:

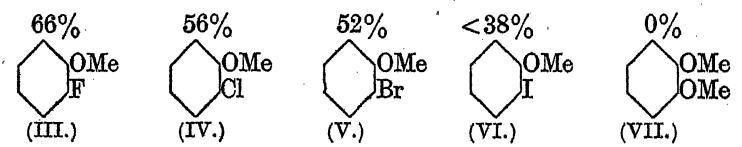


The nitration of *o*-fluoroanisole which was recorded in Part VI (*ibid.*, p. 1328) provided a still more striking example (III) of vicinal substitution in a nucleus *o*-disubstituted with *op*-orienting groups, and in Part VII (*ibid.*, p. 1685) the hypothesis was advanced that, in general, the proportion of *v*-substitution is a function of the disparity between the polar activities of the groups. It was suggested, as a possible explanation, that in an unbalanced system in which the reaction phases are determined almost wholly by one group, the second group may regulate the relative importance of these by controlling the displacement of valency-electrons past the points more directly under its influence.

An opportunity for testing this matter appeared to be provided by the recorded observations on the substitution of the halogen derivatives of benzene. Thus the experiments of Holleman (*Rec. trav. chim.*, 1915, **34**, 204) and Swarts (*ibid.*, **35**, 131) on the nitration of *o*- and *p*-dihalogenobenzenes indicate the sequence F<Cl,Br<I for the *op*-directive powers of the halogens; and although (owing to the mutual interference of the groups) caution is necessary in generalising from such observations when the directive powers of the groups are close together (as with Cl and Br), the complete sequence F<Cl<Br<I is indirectly confirmed by the regular gradation of the nuclear reactivity of the monohalogenobenzenes (Olivier, *ibid.*, 1914, **33**, 244; and unpublished observations by Miss F. R. Shaw), and of the dipole moment of comparable mono- and di-halogeno-derivatives (Höjendahl, *Nature*, 1926, **117**, 896; Errera, *Compt. rend.*, 1926, **182**, 1623).

The methoxyl group is more strongly *op*-orienting even than iodine (see below), and hence the above sequence can be expanded to F<Cl<Br<I<OMe. Therefore, if the circumstances regulating vicinal substitution have been correctly conceived, the successive introduction of these groups into the *o*-position of anisole should produce a series of substances which, taken in order, should show diminishing *v*-substitution. Since the proportion of *v*-nitration of *o*-fluoroanisole has been shown to be 66% (Part VI),* whilst that of veratrole (VII) is 0%, the other *o*-halogenoanisoles should fall into their places between these limits.

No support for this deduction was forthcoming from the literature. The nitration of *o*-chloroanisole has been investigated successively by Fischli (*Ber.*, 1878, **11**, 1463), Reverdin (*Ber.*, 1896, **29**, 2598), and Reverdin and Eckhard (*Ber.*, 1899, **32**, 2622), all of whom describe the 4-nitro-derivative, but none mentions the formation of any by-product. Reverdin also nitrated *o*-bromoanisole (*loc. cit.*) and *o*-iodoanisole (*ibid.*, p. 997), but in neither case observed the formation of any isomeride of the 4-nitro-compound. We therefore re-investigated the nitration of all these substances, and are able to show that the 6-nitro-compounds also are formed, and that the proportions of vicinal substitution fit into the series as is shown in the following formulæ (IV, V, VI):



(III.) (IV.) (V.) (VI.) (VII.)

Since the total proportions of the 3- and 5-isomerides oriented by the halogen atoms are only of the order of 2—3% (see experimental portion), the diminishing vicinal substitution in the above series is accompanied by a closely corresponding increase in substitution para to the methoxyl group.

Experimental.

Nitration of o-*Chloroanisole.*—A cooled solution of 3·1 g. of nitric acid (*d* 1·5) in acetic anhydride (12 c.c.) was very slowly added to a solution of *o*-chloroanisole (10 g.) in acetic anhydride (40 c.c.), which was cooled in ice and mechanically stirred. When the addition was complete, the solution was allowed to warm to the laboratory temperature and to remain thereat for several hours,

* A still more extreme case of *v*-substitution can be foreseen in *o*-fluoroacetanilide, which has not yet been investigated, but should yield slightly more than 66% of the 6-nitro-derivative under the conditions used in this investigation and in Part VI.

after which the solvent was removed by distillation under reduced pressure. Distillation of the product yielded 0·8 g. of unchanged *o*-chloroanisole, b. p. about 100°/13 mm. (Found: C, 56·5; H, 4·8. Calc.: C, 56·2; H, 4·9%), and 0·5 g. of undistillable residue, probably dinitro-derivatives, the whole of the remainder being a mixture of mononitro-derivatives (Found: C, 44·9; H, 3·2; N, 7·7. Calc.: C, 44·8; H, 3·2; N, 7·5%) having b. p. 125—165°, which is the b. p. range of an artificial mixture of 4- and 6-nitro-2-chloroanisoles (see below).

The mononitro-derivatives were boiled under reflux with 5% sodium hydroxide for 1 hour, preliminary experiments having shown that the labile isomerides (3- and 5-) are completely decomposed under these conditions and that the reagent is without action on the 4- and 6-nitro-compounds. The latter were extracted with ether, the aqueous solution was acidified with dilute nitric acid, and the nitroguaiacols were extracted with the same solvent. The chloride ion was then estimated either gravimetrically or volumetrically. The values in three separate nitrations were 1·64%, 1·61%, and 1·50%. The yield of mixed nitroguaiacols isolated by extraction with ether from the combined aqueous solutions obtained in the three experiments was equivalent to 1·4% of converted chloronitroanisoles, that is, the yield was 89% on the basis of the chloride estimations. Distillation in steam yielded a yellow solid which when crystallised from water gave a small amount of 3-nitroguaiacol, m. p. 61°, identified by direct comparison; and crystallisation of the original mixture yielded 5-nitroguaiacol, which was similarly identified.

The mixture of 4- and 6-nitro-compounds contained in the ethereal extract from the alkaline solution was analysed by the freezing-point method either directly or after distillation (b. p. as before), preliminary experiments having shown that operations corresponding with those described above do not affect the results obtained.

For the construction of the f. p. diagram, 2-chloro-4-nitroanisole (m. p. 95°) was prepared and purified as described by Reverdin. 2-Chloro-6-nitroanisole was obtained by Holleman (*Rec. trav. chim.*, 1915, **35**, 14) from 2 : 3-dichloronitrobenzene and sodium methoxide, but this method being unsuitable for the preparation of quantities sufficient for our purpose, the following process was evolved. *o*-Chlorophenol was added slowly to mechanically stirred, dilute nitric acid (1 : 3), and the mixture kept over-night at the ordinary temperature. The solid product was then collected, washed with water, and distilled in steam; from the distillate, bright yellow needles of 2-chloro-6-nitrophenol, m. p. 70° (softening at 65°),

separated. This was methylated with a large excess of methyl sulphate and dilute alkali by prolonged mechanical shaking at 40°. The product was collected, washed with sodium or ammonium hydroxide until colourless, and crystallised several times from aqueous alcohol; m. p. 56° (Found: C, 44·9; H, 3·4. Calc.: C, 44·8; H, 3·2%).

The freezing points were taken by the usual method in a double-jacketed tube, provided with arrangements for stirring and seeding, and surrounded by a water-bath, which was also stirred and kept at an approximately constant level well above the substance under examination. The rate at which the temperature was allowed to fall was always close to 0·3° per minute, and the maximal temperatures attained during freezing were accepted as valid readings provided that (*a*) the rise from the preceding minimum was close to 0·5°, (*b*) separation of solid with falling temperature but without total solidification did not take place. Temperatures were not corrected, but all were taken under the conditions mentioned on the same thermometer, which was graduated in fifths of a degree and could be read to tenths or less. The following values were obtained for mixtures of 2-chloro-4-nitroanisole and 2-chloro-6-nitroanisole:

2-Chloro-4-nitroanisole.	F. p.	2-Chloro-4-nitroanisole.	F. p.	2-Chloro-4-nitroanisole.	F. p.
100·0%	94·0°	66·3%	72·9°	30·1%	34·8°
91·7	89·3	61·0	71·0	28·9	37·9
86·5	86·6	56·9	67·5	26·2	39·9
82·5	84·0	53·2	64·7	24·0	41·1
78·9	81·9	47·1	58·0	20·0	43·0
76·6	80·0	42·8	52·6	16·5	44·6
73·9	79·0	38·1	47·0	13·0	47·0
72·1	77·5	34·3	42·0	8·3	48·8
68·4	76·0	31·8	38·5	0·0	53·3

These figures lie on a two-branch curve showing a eutectic, f. p. 34·8°, containing 30·1% of the 4-nitro-isomeride.

The f. p.'s of samples of mixed 4- and 6-nitro-compounds obtained in independent nitrations were 53·9° and 51·2°, which correspond with 43·2 and 41·3%, respectively, of the 4-nitro-derivative, since in each case the addition of small amounts of this compound raised the f. p. Another sample, f. p. 54·2°, corresponding with 43·8% of the 4-nitro-compound, on treatment with 22, 34, and 49% of its weight of the 6-nitro-derivative, had f. p.'s 44·7°, 40·8°, and 36·8°, respectively, which agree closely with the curve.

The most probable values of the proportions of the isomerides to the nearest unit % are therefore: 4-nitro, 42%; 6-nitro, 56%; 3- plus 5-nitro-, 2%.

The value for the 4-nitro-compound was confirmed by separation after the destruction of the 3- and 5-nitro-derivatives. The mixture

of the 4- and 6-nitro-compounds (10·00 g.) was fractionally crystallised from dilute alcohol, 32% of the pure 4-derivative being obtained. The combined residues had f. p. 46° on the branch of the f. p. curve in which the solid phase is the 6-nitro-isomeride. It follows that both isomerides can be qualitatively separated by crystallisation from dilute alcohol, followed by partial solidification of the fused residues. The above f. p. corresponds with 15% of the 4-nitro-compound, so that the quantity originally present was $32 + (0{\cdot}15 \times 68) = 42{\cdot}2\%$ of the binary mixture, that is, 41·6% of the original nitration product.

Nitration of o-*Bromoanisole.*—These experiments were so similar to the preceding series that only the more important differences need be mentioned.

Boiling with alkali for 4 hours was carried out to ensure complete destruction of the 3- and 5-nitro-compounds.

2-Bromo-6-nitrophenol, m. p. 65°, which was prepared in the same way as its chloro-analogue, could not be methylated conveniently with methyl sulphate, and was therefore converted into its silver salt, which was heated under reflux with a large excess of methyl iodide dissolved in benzene. Final purification was effected as in the case of the chloro-compound. M. p. 66°.

The whole of the f. p. curve of the 4- and 6-nitro-compounds was not plotted, but only a portion containing the f. p. of the nitration mixture on each branch and the eutectic. It was found convenient to allow a slightly higher rise of temperature on freezing, and 1·0° was the standard taken.

The results were as follows: The products from two independent nitrations yielded bromide ion corresponding with 2·70 and 2·67%, respectively, of the 3- plus 5-isomerides, and the yield of mixed nitroguaiacols was 85% calculated on this basis. The f. p. curve used for analysis of the mixture of the 4- and 6-nitro-compounds was based on the following f. p. observations:

2-Bromo-4-nitroanisole.	F. p.	2-Bromo-4-nitroanisole.	F. p.	2-Bromo-4-nitroanisole.	F. p.
0·0%	64·3°	23·7%	49·4°	36·9%	52·0°
7·1	59·6	25·2	47·1	42·2	56·2
13·3	55·7	27·3	46·8	43·4	57·5
17·7	52·8	29·7	46·8	45·8	60·0
20·2	50·9	32·2	48·3	50·5	65·0

The curve contains two rectilinear branches intersecting at 29% of the 4-nitro-compound, the corresponding f. p. being 45·5°. The binary mixtures obtained from two nitration experiments had f. p.'s 60·0° and 61·8°, indicating, respectively, 46·0 and 47·5% of the 4-nitro-derivative, since additions of small amounts of this isomeride to the first sample showed the f. p. to be on the corresponding

branch of the curve. The second sample was mixed with the exact quantity of the 6-nitro-isomeride calculated to change the composition to that of the eutectic. The f. p. was then 45·0° and the addition of further small quantities of the 6-nitro-compound raised this.

The most probable values of the proportions of the isomerides to the nearest unit % are therefore: 4-nitro-, 45%; 6-nitro-, 52%; 3- plus 5-nitro-, 3%.

Nitration of o-Iodoanisole.—*o*-Iodoanisole was nitrated in acetic anhydride solution (*a*) under the conditions used for the analogous chloro- and bromo-compounds, (*b*) at greater dilutions, (*c*) at a lower temperature, — 10° to — 5°. In each case, a small amount of iodine was liberated which afterwards became reabsorbed. For this reason, and also because it was not found possible selectively to destroy the 3- and 5-nitro-compounds by alkalis or bases (despite numerous exploratory experiments with *o*-iodonitrobenzene), we were unable to study the nitration product quantitatively. Reverdin (*loc. cit.*) isolated 60% of the 4-nitro-compound from his nitration product, and we therefore endeavoured to isolate as much as possible of this isomeride by his method. From the products of two independent nitrations we obtained 62% and 58%, respectively, of this isomeride, but the residues could not be separated.

THE UNIVERSITY, LEEDS. [*Received, May 11th*, 1927.]

CCXVII.—*Investigations in the Diphenyl Series. Part VI. The Configuration of Diphenyl Derivatives.*

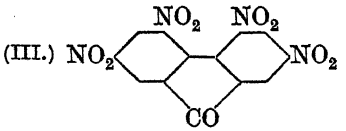
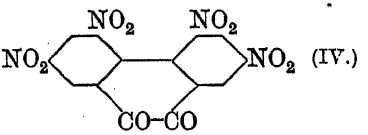
By FRANK BELL and PERCY HARRY ROBINSON.

THE normal and the acid quinine salt of 4-nitrodiphenic acid can be crystallised without showing any sign of resolution. 6-Nitrodiphenic acid is readily resolvable, and the optical activity is apparently of a normal degree of permanence. This striking difference in behaviour of two such similarly constituted acids can be accounted for only by the assumption that the presence of the nitro-group in position 6 is essential to prevent the interchange

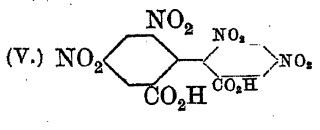
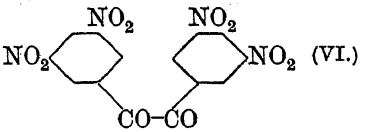


of the enantiomorphs (I) and (II). The fact that it has so far proved impossible to prepare tetranitrofluorenone (III) or tetra-

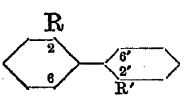
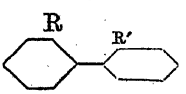
nitrophenanthraquinone (IV), whilst diphenic acid and benzil readily yield tetranitro-derivatives (V and VI), could be anticipated

(III.)  (IV.) 

from this "obstacle" theory. Moreover, it would be expected that diphenic acids unsubstituted in the 6 : 6′-positions should

(V.)  (VI.) 

form anhydrides, in spite of many statements to the contrary (*e.g.*, Adkins, Steinbring, and Pickering, *J. Amer. Chem. Soc.*, 1924, **46**, 1918; Underwood and Kochmann, *ibid.*, p. 2069). It is now found that 4-nitro- and 4 : 4′-dinitro-diphenic acids yield anhydrides under suitable conditions; an attempt to prepare the anhydride of 6-nitrodiphenic acid was, however, unsuccessful. According to the present hypothesis, a diphenyl derivative with two sufficiently large groups in the 2- and 2′-positions, that is, groups which, owing to size or electrical character, are unable to pass the 6′- and 6-positions, respectively, should be capable of resolution

(VII.)   (VIII.)

(VII and VIII). Suitable derivatives for testing this point have not yet been obtained. The dicamphorsulphonyl derivative of 2 : 2′-diaminodiphenyl was a viscous mass, and the camphor(and bromocamphor)-sulphonates of several 2 : 2′-derivatives of tetramethylbenzidine proved unsuitable for crystallisation. Menthyl hydrogen and di-*d*-β-octyl diphenates were not obtained in a solid condition, but dimenthyl and *d*-β-octyl hydrogen diphenates were crystallised from several solvents without showing any indication of resolution. The resolvability of such compounds is therefore still an open question.

EXPERIMENTAL.

Optically Active 6-Nitrodiphenic Acid.—Morphine hydrate (7·7 g.) was added to a boiling solution of 6-nitrodiphenic acid (7·2 g.) in alcohol (500 c.c.). The precipitated salt (7·8 g.; m. p. 224°) (Found: C, 63·6, 63·7; H, 5·4, 5·3%. $[\alpha]_{5461}$ −87·5° in pyridine,

$c = 4{\cdot}99$; $l = 2{\cdot}0$) was extracted repeatedly with boiling alcohol, and the product ($[\alpha]_{5461}$ $-91{\cdot}5°$ in pyridine; $c = 4{\cdot}81$; $l = 1{\cdot}0$) was dissolved in a large bulk of boiling water and decomposed with a slight excess of hydrochloric acid. The solution was extracted with ether, and the extract was repeatedly washed with dilute hydrochloric acid, dried with sodium sulphate, and then evaporated to dryness. The residue was further purified by reprecipitation from solution in ammonia by hydrochloric acid. The *d* + *dl*-6-nitrodiphenic acid melted indefinitely at 240—245°, and had $[\alpha]_{5461}$ $+56{\cdot}2°$ ($c = 5{\cdot}91$; $l = 1{\cdot}0$) in absolute ethyl alcohol.

The alcoholic mother-liquor containing the more soluble salt ($[\alpha]_{5461}$ $-84{\cdot}6°$ in pyridine solution; $c = 5{\cdot}0$, $l = 1{\cdot}0$) was concentrated and poured into dilute hydrochloric acid, and the precipitated *l* + *dl*-acid recovered as described above. The *l* + *dl*-acid melted at 239—245° and had $[\alpha]_{5461}$ $-66{\cdot}7°$ in ethyl alcohol ($c = 5{\cdot}07$; $l = 1{\cdot}0$). Quinine hydrogen 6-nitrodiphenate was equally suitable and after one crystallisation gave on decomposition the *d* + *dl*-acid with $[\alpha]_{5461}$ $+62°$.

The acid ($[\alpha]_{5461}$ $-66{\cdot}7°$) was dissolved in boiling acetic acid and allowed to crystallise slowly. The acid which crystallised had $[\alpha]_{5461}$ $-57{\cdot}6°$, whilst the mother-liquor, on evaporation to dryness, gave an acid with $[\alpha]_{5461}$ $-60{\cdot}3°$. Solutions of four different samples of acid having $\alpha_{5461} = -1{\cdot}12°$, $-2{\cdot}90°$, $-3{\cdot}38°$, and $+3{\cdot}32°$ respectively in absolute ethyl alcohol were left in corked flasks at laboratory temperature for 6 months; they then had the values $\alpha_{5461} = -1{\cdot}11°$, $-2{\cdot}92°$, $-3{\cdot}24°$, and $+3{\cdot}24°$, respectively.

Dichloride of 4-Nitrodiphenic Acid.—The acid was added slowly to warm thionyl chloride, and the resultant solution evaporated to dryness in a vacuum. The residual solid crystallised from benzene–light petroleum as a pale yellow powder, m. p. 90—92° (Found: C, 52·6; H, 2·1. $C_{14}H_7O_4NCl_2$ requires C, 51·8; H, 2·2%).

4-Nitrodiphenic Anhydride.—Thionyl chloride was added drop by drop to 4-nitrodiphenic acid, and the resultant solution evaporated to dryness in a vacuum. The residual solid crystallised from acetic anhydride in small needles, m. p. 205—207° (Found: C, 62·8; H, 2·4. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6%).

4 : 4′-Dinitrodiphenic Anhydride.—4 : 4′-Dinitrodiphenic acid (1·9 g.) and its acid chloride (2·1 g.) were heated under reflux with acetic anhydride for several hours. On cooling, the liquid filled with small prisms, which sintered at 125° and melted at 232—234° (Found: C, 51·9; H, 3·0; loss on drying to constant weight at 130°, 24·3. $C_{14}H_6O_7N_2,C_4H_6O_3$ requires C, 51·9; H, 2·9; loss, 24·5%). After crystallisation from benzene, the anhydride formed

a powder, m. p. 233—235° (Found: C, 54·1; H, 2·1. $C_{14}H_6O_7N_2$ requires C, 53·5; H, 1·9%).

Dichloride of 6-Nitrodiphenic Acid (compare 4-nitrodiphenic acid).—This was a pale yellow powder, m. p. 87° (Found: C, 51·8; H, 2·2. $C_{14}H_7O_4NCl_2$ requires C, 51·8; H, 2·2%). Attempts to prepare the anhydride of this acid resulted in viscous products only.

2 : 2′-*Dibenzamidotetramethylbenzidine*, prepared by interaction of the components in pyridine, separated from benzene as a crystalline powder, m. p. 201° (Found: C, 75·9; H, 6·1. $C_{30}H_{30}O_2N_4$ requires C, 75·3; H, 6·3%), and 2 : 2′-*di*-p-*toluenesulphonylamidotetramethylbenzidine*, similarly prepared, crystallised from alcohol in leaflets, m. p. 203° (Found: C, 62·8; H, 5·8. $C_{30}H_{34}O_4N_4S_2$ requires C, 62·3; H, 5·9%).

2-*Aminotetramethylbenzidine*, prepared by the same method as 2 : 2′-diaminotetramethylbenzidine, crystallised from alcohol in plates, m. p. 138° (Found: C, 74·8; H, 7·8. $C_{16}H_{21}N_3$ requires C, 75·3; H, 8·2%).

d-β-*Octyl hydrogen diphenate*, prepared from diphenic anhydride and *d*-β-octanol in the usual way, formed large needles, m. p. 70—73°, when crystallised from light petroleum (Found: equiv., 349. $C_{22}H_{26}O_4$ requires equiv., 354). It was unchanged in rotatory power ($[\alpha]_D$ +51°; $c = 5·0$; $l = 1·0$ in absolute ethyl alcohol) by recrystallisation from light petroleum or aqueous ethyl alcohol.

Dichloride of Diphenic Acid.—Diphenic acid (20 g.) was dissolved in warm thionyl chloride (100 c.c.), and the excess of thionyl chloride then removed in a vacuum. The residue was boiled with benzene, and the solution was filtered from diphenic anhydride (2—3 g.) and diluted with light petroleum. A yield of 80% of the dichloride, m. p. 97°, was obtained.

Dimenthyl Diphenate.—(*a*) A solution of equivalent quantities of menthol and diphenic acid dichloride in ether was boiled for 15 hours in the presence of potassium carbonate. Water was then added and the ethereal layer was separated, dried, and evaporated. The oily residue was dissolved in light petroleum, from which it separated in plates (yield 30%), m. p. 123—126°, $[\alpha]_{5461}$ −118·6°, which, after recrystallisation from light petroleum, had m. p. 126° and $[\alpha]_{5461}$ −120·4° in chloroform solution ($c = 4·88$, $l = 2·0$) (Found: C, 78·5; H, 8·3. $C_{34}H_{46}O_4$ requires C, 78·7; H, 8·9%). (*b*) A solution of equivalent quantities of menthol and diphenic acid dichloride in pyridine, after standing for 12 hours, was poured into water, and the resulting precipitate crystallised from light petroleum. Successive crops had $[\alpha]_{5461}$ −119·6°, −119·2°, −119·0° (yield 60%),

and after recrystallisation from light petroleum or acetic acid the ester had $[\alpha]_{5461}$ −120·3° ($c = 4{\cdot}94$, $l = 2{\cdot}0$).

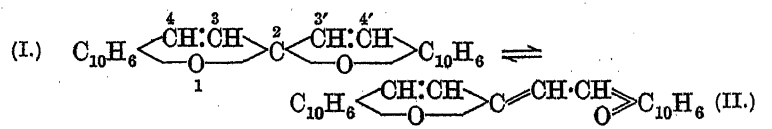
One of the authors (F.B.) is in receipt of a grant from the Department of Scientific and Industrial Research.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, May 11th*, 1927.]

CCXVIII.—*Styrylpyrylium Salts. Part IX. Colour Phenomena associated with Benzonaphtha- and Dinaphtha-*spiro*pyrans.*

By ROBERT DICKINSON and ISIDOR MORRIS HEILBRON.

IN a previous communication (this vol., p. 14) a preliminary account was given of the remarkable property exhibited by di-β-naphtha-*spiro*pyran of forming in cold inert solvents colourless solutions which develop an intense violet-blue colour on heating; on cooling, the colour disappears and the substance may be recovered unchanged. This phenomenon, which may be repeated any number of times, we tentatively suggested might be accounted for by intramolecular change from the *spiro*-type (I) to the ortho-quinonoid system (II), a view which has been advanced by Löwenbein and

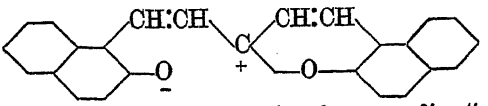


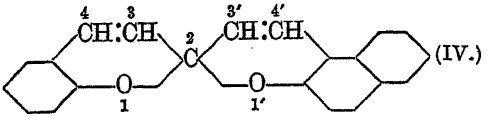
(I.) (II.)

Katz also (*Ber.*, 1926, **59**, 1377), who almost simultaneously observed the same effects in the case of the 3-methyl, phenyl, and benzyl derivatives of the above compound.

On the other hand, Dilthey, Berres, Hölterhoff, and Wübken (*J. pr. Chem.*, 1926, **114**, 179), who have also examined this phenomenon, reject the quinonoid hypothesis on the grounds that (i) whereas true quinones mostly show a bathochromic effect in piperidine solution and never a hypsochromic action, di-β-naphtha-*spiro*pyran gives only a yellow solution which is unaffected by heat (compare Dilthey and Wizinger, *Ber.*, 1926, **59**, 1856), and (ii) neither dibenzo*spiro*pyrans nor mixed benzo-β-naphtha*spiro*pyrans show any alteration in colour either on melting or in solvents, although quinone formation is equally possible in both cases. They conclude that the appearance of colour is due to ionic dissociation, the

coloured form being represented as a heteropolar molecule of the type (III):

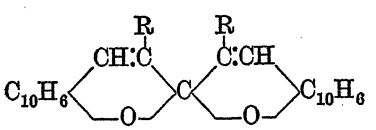
(III.) 



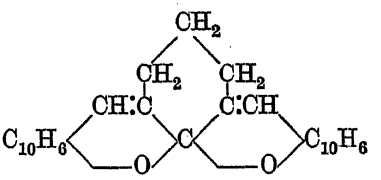
The possibility of the phenomenon being due to free radical formation has been considered by Löwenbein and by Dilthey, both concluding that such a view is incorrect. Dilthey treated a hot solution of di-β-naphtha*spiro*pyran in chlorobenzene with a stream of oxygen for an hour, and was unable to detect any change; a similar result was obtained with hydrogen. These two experiments show the absence of tervalent carbon and univalent oxygen, respectively. We have repeated the former, and also, on passing oxygen through a solution of the compound in toluene at 100°, could not detect any change, even after 15 hours' treatment. Further, we find that the colour is unchanged by the addition of quinol, a reagent which almost instantaneously reduces all the known types of radicals, with disappearance of the colour (compare Ingold, *Ann. Rep.*, 1924, **21**, 115—121). In addition, both Löwenbein and Dilthey have definitely shown that the molecular weights of these compounds are normal, whether the solution is coloured or not.

We have now made a very extensive examination of various *spiro*pyrans, and whereas we are in agreement with Dilthey that the colour effect is ionic in character, it will be shown that other factors enter into the case. In the first place, we have prepared *benzo*-β-*naphtha*spiro*pyran* (IV) by the acid condensation of 2-naphthol-1-aldehyde with *o*-hydroxystyryl methyl ketone, followed by hydrolysis of the resulting styrylpyrylium salt, and find that it exhibits, contrary to Dilthey's generalisation, the characteristic colour changes in solution, a wine-red colour being developed in hot solvents. We have also prepared the 3- and 3′-*methyl* derivatives of (IV). The former was obtained by condensing 2 : 3-dimethylbenzopyrylium chloride (Decker and Fellenberg, *Annalen*, 1909, **364**, 26) with 2-naphthol-1-aldehyde and resembles the parent benzo-β-naphtha*spiro*pyran in all respects, giving a deep red solution in boiling xylene and melting to a reddish-purple liquid. On the other hand, the isomeric 3′-*methylbenzo*-β-*naphtha*spiro*pyran*, the preparation of which from the condensation of 2-naphthol-1-

aldehyde with *o*-hydroxystyryl ethyl ketone definitely fixes its structure, gives no coloured solutions in boiling solvents, nor does it melt to a coloured liquid. This compound is undoubtedly identical with that obtained by Dilthey and his co-workers (*loc. cit.*), who, however, from their method of preparation were unable definitely to fix its constitution. We have also prepared 3 : 3′-*dimethyldi*-β-*naphtha*spiro*pyran* (V), *ethyl di*-β-*naphtha*spiro*pyran*-3 : 3′-*dicarboxylate* (VI), and 3 : 3′-*trimethylenedi*-β-*naphtha*spiro*pyran* (VII), none of which gives rise to highly coloured solutions.



(V, R = CH_3; VI, R = CO_2Et.)

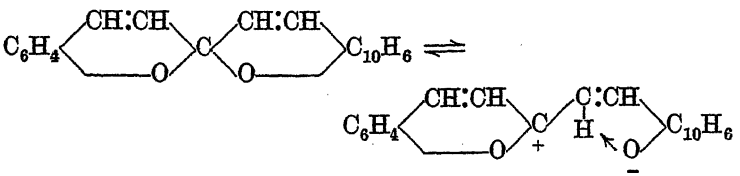


(VII.)

These experiments taken in conjunction with the work of Löwenbein and Katz (*loc. cit.*) lead to the conclusion that the conditions necessary for colour development are not wholly governed, as stated by Dilthey and his co-workers (*loc. cit.*), by the loading of the *spiro*pyran with two naphthalene nuclei, but that the determining factors are (a) *at least one naphthalene nucleus must be present* and (b) *the* 3′-*carbon atom in the naphthapyran ring must be unsubstituted.*

The obvious deduction to be drawn from (a) is that the ionised molecule arises through scission of the naphthapyran ring. Furthermore, when it is considered that the system thus produced contains a strongly polar, conjugated group, $\bar{O}—C=C—\overset{4'}{C}H=\overset{3'}{C}H—\overset{+}{R}$ (in which R represents the positively charged pyran residue), it will be seen that conditions peculiarly conducive to co-ordinated ring formation exist. In this connexion, factor (b) becomes operative. In the first place, it definitely proves that the quinonoid formulation fails to account for the observed facts. Secondly, it follows that, so long as the 3′-carbon atom in the benzo-β-naphtha*spiro*pyrans is unsubstituted, "chelate" formation can readily occur, but that this process is absolutely precluded when any other group is substituted for the free hydrogen atom. The same condition holds for the di-β-naphtha*spiro*pyrans: here the positions 3 and 3′ are identical, but at least one of them must be unsubstituted. The cumulative experimental evidence has consequently forced us to the conclusion that the colour development is the result of a series of changes in which equilibrium is established between the neutral

*spiro*pyran and an ionised " chelate " compound, as represented by the following formulæ:



We are extending this investigation to include the influence of substitution in the 4- and 4′-positions of the *spiro*pyran nucleus. It remains to be mentioned that we have so far failed to obtain a pyrylium salt or *spiro*pyran by the condensation of 2-naphthol-1-aldehyde with dibenzyl ketone; two compounds have been isolated, the constitutions of which are under investigation.

Experimental.

*Benzo-β-naphtha*spiro*pyran* (IV).—A solution of 2-naphthol-1-aldehyde (5 g.) and 2-hydroxystyryl methyl ketone (5 g.) in alcohol (40 c.c.) was treated with 60% perchloric acid solution (9 c.c.), saturated with dry hydrogen chloride, and kept for 3 days at 0°. The separated crystalline solid was then washed with ether, and shaken with concentrated ammonia in presence of excess of ether until it had dissolved. After being washed and dried, the dark ethereal solution was concentrated. The crystalline crust which separated was recrystallised first from ether, then twice from acetone with charcoal, and finally from aqueous acetone. The spiro*pyran* was obtained in small, colourless, glistening plates; these darkened at about 160° and melted at 168—169° to a deep purple liquid which very slowly resolidified, on cooling, with gradual fading of the colour.

The *spiro*pyran is soluble in concentrated sulphuric acid, giving a ruby-red solution, and develops with boiling alcoholic sodium hydroxide a purplish-red colour. Its colourless solutions in acetone, benzene, and xylene become wine-red on heating, the colour disappearing again on cooling. On warming with alcohol, a similar colour develops, but it is more purple, and is still more so when water is added to the solution (Found: C, 84·4; H, 4·4. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%).

3′-*Methylbenzo-β-naphtha*spiro*pyran*.—Perchloric acid (8 c.c. of 60%) was added to a solution of 2-naphthol-1-aldehyde (5 g.) and 2-hydroxystyryl ethyl ketone (5 g.) in alcohol (40 c.c.), and the whole saturated with hydrogen chloride. The separated microcrystalline perchlorate was washed with ether, suspended in benzene,

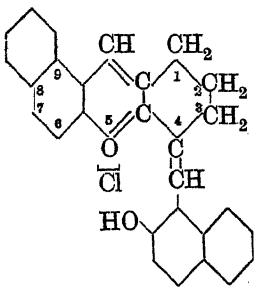
and treated with a few drops of concentrated ammonia. Water was then added and the benzene solution was separated, dried, and, after concentration, treated with light petroleum, whereupon crystals slowly separated (yield, about 2·5 g.). These were twice recrystallised from absolute alcohol (charcoal), finally being obtained in clusters of colourless, silky needles, m. p. 177—178° (Dilthey, *loc. cit.*, describes pale yellowish needles, m. p. 174°). This *spiro*pyran shows no colour change when heated with inert solvents, such as xylene. In concentrated sulphuric acid, the solution is orange-red (Found: C, 84·2; H, 5·3. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%).

3-*Methylbenzo*-β-*naphtha*spiro*pyran*.—A solution of salicylaldehyde (2 g.) and methyl ethyl ketone (1·2 g.) in glacial acetic acid (6 c.c.) was saturated with hydrogen chloride and kept for a few hours to enable the primary condensation to become complete; 2-naphthol-1-aldehyde (2·9 g.), dissolved in acetic acid (9 c.c.), was then added, the colour changing from red to purple. After 12 hours, ether was gradually added, the pyrylium chloride slowly crystallising. This was collected, washed with ether, and shaken in ethereal suspension with an aqueous solution of sodium acetate until the colour was discharged. The ethereal solution, after being washed, dried, and concentrated, deposited pale greenish-yellow prisms, which were recrystallised first from ether and then from acetone, giving faintly greenish-yellow prisms. These darkened at 145° and melted at 149° to a purple liquid; on cooling, the colour faded but did not disappear completely until the substance had solidified, after several days. Colourless solutions of the *spiro*pyran in acetone, xylene, etc., become wine-red on heating, the colour disappearing again on cooling. Its ruby-red solution in concentrated sulphuric acid is faintly fluorescent (Found: C, 84·5; H, 5·3. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%).

3 : 3′-*Dimethyldi*-β-*naphtha*spiro*pyran* (V).—A hot solution of 2-naphthol-1-aldehyde (2·1 g.) and diethyl ketone (1 c.c.) in glacial acetic acid (10 c.c.) was saturated with hydrogen chloride. After the mixture had been kept at 0° for several days, a small amount of the pyrylium chloride separated in green needles. These were removed, and the mother-liquor was treated with excess of perchloric acid; chocolate-brown needles of the salt slowly separated. Both products were dissolved in acetone (the chloride giving a violet and the perchlorate a dark red solution) and, while hot, treated with dilute ammonia, drop by drop, until the colour was discharged. The spiro*pyran* crystallised from the yellow acetone solutions, either on evaporation or on the addition of water. Recrystallised from benzene, the compound separated in pale lemon-

yellow rhombs, m. p. 238° to an olive-green liquid. It does not exhibit any colour changes when heated with solvents (Found: C, 85·9; H, 5·1. $C_{27}H_{20}O_2$ requires C, 86·2; H, 5·3%).

4-2′-*Hydroxy*-1′-*naphthylidene*-1 : 2 : 3 : 4-*tetrahydro*-8 : 9-*benzoxanthylium Chloride* (annexed formula).—A solution of 2-naphthol-1-aldehyde (5 g.) and *cyclo*hexanone (2 c.c.) in alcohol (50 c.c.) was saturated with hydrogen chloride and kept for 12 hours at 0°. The separated crystalline solid (yield, 95%) was washed with ether and recrystallised from absolute formic acid previously saturated with hydrogen chloride. The salt separated in dark brown, glistening needles, insoluble in water and sparingly soluble in alcohol to a reddish-purple solution. In concentrated sulphuric acid its colour is orange-red (Found: C, 74·1; H, 5·2; Cl, 7·4. $C_{28}H_{21}O_2Cl,HCO_2H$ requires C, 74·0; H, 4·9; Cl, 7·5%).



3 : 3′-*Trimethylenedi*-β-*naphtha*spiro*pyran* (VII).—The above-mentioned salt (2 g.), suspended in boiling alcohol (50 c.c.), was treated with sodium acetate, the heating being continued until the colour of the pyrylium salt was discharged, a curdy, greenish-yellow solid separating. After drying, this was twice crystallised from benzene, separating in minute, sulphur-yellow rhombs, m. p. 233—234° (decomp.). The yellow benzene solution exhibits a fine green fluorescence. The spiro*pyran* is not appreciably soluble in alcohol, and does not fluoresce in concentrated sulphuric acid. A cherry-red colour slowly develops on prolonged boiling with alcoholic potash. This *spiro*pyran does not exhibit any colour changes on heating in solvents (Found: C, 86·5; H, 5·4. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·2%).

Ethyl Di-β-*naphtha*spiro*pyran*-3 : 3′-*dicarboxylate* (VI).—A solution of 2-naphthol-1-aldehyde (2 g.) and ethyl acetonedicarboxylate (1·2 g.) in hot alcohol (12 c.c.) was saturated with hydrogen chloride, and the passage of the gas was maintained until the solution was cold. After 2 days, the dark, crystalline deposit was washed with ether, suspended in hot acetone (which became bright red), and treated with dilute ammonia drop by drop until the colour was discharged. Alternatively, the pyrylium salt may be suspended in ether and hydrolysed by shaking it with aqueous sodium acetate, but the former method is preferred. The acetone solution, after being filtered, was treated with water until crystallisation ensued. Recrystallised from acetone, or benzene and light petroleum, the spiro*pyran* formed pale sulphur-yellow rhombs, m. p. 205—207°. It is very stable to hydrolysing agents, resisting the action of

alcoholic potash, but with acids it readily reverts to the pyrylium salt (Found: C, 75·5; H, 4·9. $C_{31}H_{24}O_6$ requires C, 75·6; H, 4·9%).

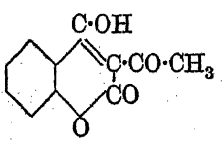
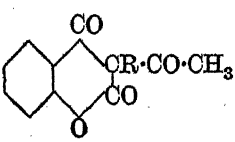
We desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) which enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, May 27th*, 1927.]

CCXIX.—*The Preparation of 4-Hydroxycoumarin Derivatives.*

By ISIDOR MORRIS HEILBRON and DOUGLAS WILLIAM HILL.

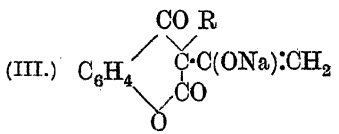
THE hydroxycoumarins here described were prepared as a preliminary to the study of their action on aryl magnesium compounds, details of which will be furnished in subsequent papers. 4-Hydroxycoumarin (benzotetronic acid) was first described by Anschütz (*Annalen*, 1909, **367**, 169), who prepared it by condensing sodioacetoacetic ester with *o*-acetoxybenzoyl chloride in ethereal solution, followed by hydrolysis of the primarily isolated 3-acetyl-4-hydroxycoumarin (I). We have now obtained the substituted 3-methyl-, 3-benzoyl-, and 3-benzyl-4-hydroxycoumarins in good yield by this method. The 3-phenyl derivative has not been examined, as it has already been obtained by Pauly and Lockemann (*Ber.*, 1915, **48**, 28) by the intramolecular condensation of methyl *o*-phenylacetoxybenzoate in presence of sodium at 160°. Employing the α-substituted acetoacetic esters, we expected to obtain the acetyl derivatives (II) on removal of solvent from the condensation mixture; the products, however, were sodium salts, from which the acetyl-free hydroxycoumarins were obtained when their respective aqueous solutions were acidified.

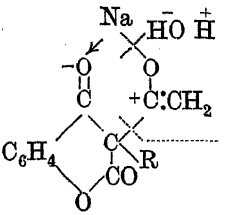
(I.)  (II.) 

(R = CH_3, COPh, or CH_2Ph)

The extraordinarily ready elimination of acetyl is at first sight somewhat anomalous. It has been shown, however, by Widmann (*Ber.*, 1902, **35**, 1153) that 3-acetylcoumarin possesses strongly acidic properties, behaving as a typical pseudo-acid, and thus by analogy the sodium compounds now obtained may be similarly represented as still containing the acetyl intact in the molecule (III).

Although offering an explanation of the formation of sodium salts, this view in itself does not explain the subsequent ease with which the acetyl group is eliminated, for obviously precisely the same effect could occur with 3-acetyl-4-hydroxycoumarin, from which, however, the acetyl radical is by no means readily eliminated, requiring indeed several hours' heating with moderately concentrated potassium hydroxide solution for its removal.

(III.) 

 (IV.)

We submit, however, that a satisfactory interpretation of the observed facts can be arrived at by assuming that in the acetyl 3-substituted benzotetronic acids the simple enol does not exist as such, but that the sodium derivatives are present as co-ordinated salts (IV) only stable in non-aqueous media. Owing to the great tendency of the negatively charged oxygen of the carbonyl group to pass into the enolic state, as evidenced by the fact that benzotetronic acid itself is a strong acid, the chelated acetyl sodium compound is disrupted by water with formation of the free hydroxycoumarin. These changes obviously do not occur with the unsubstituted 3-acetylbenzotetronic acid, for here a free hydrogen atom is available for immediate formation of the isomeric coumarin form, and consequently this compound closely resembles 3-acetylcoumarin itself in stability.

Considerable difficulty was encountered in the methylation of these 4-hydroxycoumarins. This appears to be a general characteristic of this class of compounds, as similar difficulties were met with by Sonn (*Ber.*, 1917, **50**, 1292), who obtained only very small yields of 4 : 7-dimethoxycoumarin by the action of methyl sulphate upon the 4 : 7-dihydroxy-compound, the main product being 4-hydroxy-7-methoxycoumarin. We have now, however, prepared the dimethoxy-derivative in good yield by employing diazomethane.

EXPERIMENTAL.

4-Hydroxy-3-methylcoumarin.—Ethyl methylsodioacetoacetate (from 100 g. of the ester) in ether (600 c.c.) was treated with *o*-acetoxybenzoyl chloride (46 g.), prepared by the action of thionyl chloride upon *o*-acetoxybenzoic acid, and the mixture was heated under reflux on the water-bath for 18 hours. The resultant yellow

solid was filtered off, well washed with ether, and dissolved in water, the solution was carefully neutralised with dilute sulphuric acid, and the semi-solid precipitate was crystallised repeatedly from dilute alcohol in presence of animal charcoal and finally from methyl alcohol, the *coumarin* being obtained in colourless needles, m. p. 230°, readily soluble in alcohol and somewhat sparingly soluble in ether and benzene (yield, 60%) (Found : C, 68·3; H, 4·8. $C_{10}H_8O_3$ requires C, 68·1; H, 4·6%).

4-*Methoxy*-3-*methylcoumarin* was prepared by heating the dry silver salt of the coumarin under reflux with a slight excess of methyl iodide. Silver iodide and the excess of methyl iodide were removed; the residual colourless oil slowly solidified and was then crystallised first from ether and finally from alcohol, the *methyl ether* separating in colourless needles, m. p. 89·5° (Found : C, 69·0; H, 5·4. $C_{11}H_{10}O_3$ requires C, 69·4; H, 5·3%).

4-*Hydroxy*-3-*benzylcoumarin*.—Ethyl benzylsodioacetoacetate, prepared by adding the ester (90 g.) to granulated sodium (9 g.) in xylene (90 c.c.), was boiled under reflux with *o*-acetoxybenzoyl chloride (50 g.) in ether (300 c.c.) for 24 hours. The resultant thick precipitate was filtered off and dissolved in water, and the solution rendered acid. The semi-solid mass was extracted with ether, the solution dried, and after removal of the ether the residue was crystallised from aqueous alcohol, from which the *coumarin* separated in colourless needles, m. p. 205° (Found : C, 76·1; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·7%).

4-*Hydroxy*-3-*benzoylcoumarin* was prepared in a similar manner from ethyl α-benzoylsodioacetoacetate. The *coumarin* crystallised from 96% alcohol in colourless needles, m. p. 144°, readily soluble in alcohol, less soluble in benzene and ether. It is also readily soluble in sodium carbonate solution (Found : C, 71·8; H, 3·8. $C_{16}H_{10}O_4$ requires C, 72·1; H, 3·8%).

4-*Methoxycoumarin*.—(1) A solution containing 4-hydroxycoumarin (2 g.), acetone (200 c.c.), and aqueous potassium hydroxide (16 c.c. of 20%) was gently warmed and treated with methyl sulphate (2·5 g.), added in small quantities at a time. The mixture was boiled for an hour and the 4-*methoxy*-derivative was precipitated by dilution with water and separated from a small quantity of unchanged 4-hydroxycoumarin by addition of sodium carbonate in slight excess. It crystallised from water in colourless flakes, m. p. 124° (yield, 25%).

(2) Freshly prepared nitrosomethylurea (Werner, J., 1919, **115**, 1098) (25 g.), suspended in a solution of 4-hydroxycoumarin (10 g.) in acetone (100 c.c.), was very slowly treated with concentrated potassium hydroxide solution (17 g. in 12 c.c. of water), care being

taken to prevent the reaction becoming too violent. The *methoxycoumarin* was precipitated with water and crystallised as above (yield, 40%) (Found: C, 67·9; H, 4·5. $C_{10}H_8O_3$ requires C, 68·1; H, 4·6%).

4 : 7-Dihydroxycoumarin was prepared by a slight modification of Sonn's method (*loc. cit.*), ethyl cyanoacetate being employed in place of the free acid. A better yield of the coumarin was obtained by heating the ketimine under reflux with concentrated sulphuric acid (20 c.c.) and water (40 c.c.) for 3 hours. The ketimine gradually dissolved and after some time the ketone separated; it was recrystallised from hot water; m. p. 265° (yield, 80%).

4 : 7-*Dimethoxycoumarin.*—Sonn (*loc. cit.*) obtained this compound together with a large amount of 7-methoxy-4-hydroxycoumarin by the action of methyl sulphate upon 4 : 7-dihydroxycoumarin at 0°. On repeating this work it was found that the yield of alkali-insoluble product was almost negligible. Attempts to methylate the 4-hydroxy-group with methyl iodide and sodium ethoxide or silver oxide also failed. The dimethyl ether was finally obtained in good yield by passing diazomethane into a solution of 7-methoxy-4-hydroxycoumarin (7 g.) in absolute alcohol (150 c.c.); after remaining for 3 hours at room temperature, the solution was concentrated and the dimethoxycoumarin was precipitated by dilution with water, washed with dilute alkali solution to remove unchanged 7-methoxy-4-hydroxycoumarin, and recrystallised from boiling water. It formed colourless needles, m. p. 155—156°, identical with Sonn's product (yield, 85%).

Our thanks are due to Mr. J. Kirwan, M.Sc., for help in some of the preparative work and to the Council of the Department of Scientific and Industrial Research for a grant to one of us (D. W. H.).

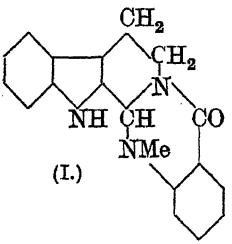
THE UNIVERSITY, LIVERPOOL. [*Received, May 27th*, 1927.]

CCXX.—*A Synthesis of Rutæcarpine.*

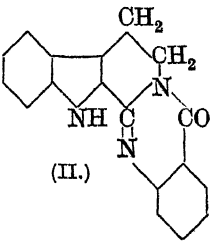
By YASUHIKO ASAHINA, RICHARD HELMUTH FRED MANSKE, and ROBERT ROBINSON.

FOLLOWING the analytical investigations (Asahina and Mayeda, *J. Pharm. Soc. Japan*, 1916, No. 416; Asahina and Fujita, *ibid.*, 1921, 863; Asahina, *ibid.*, 1924, No. 503, 1) which clearly proved that evodiamine and rutæcarpine, the alkaloids of *Evodia rutæcarpa*, Benth. and Hook., have the constitutions (I) and (II), respectively,

synthetical experiments were instituted by one of us in Japan,* whilst, on the other hand, the natural development of some work in progress at Manchester led in the same direction; the outcome is the present joint memoir, in which we describe an unexpectedly simple synthesis of rutæcarpine (II).



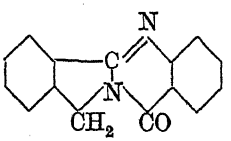
(I.)

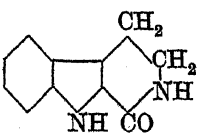


(II.)

As a preliminary we studied the preparation of a quinazolone derivative from an available cyclic amide and anthranilic acid and found that phthalimidine and methyl anthranilate readily condense in the presence of phosphorus trichloride (compare Sen and Rây, J., 1926, 646) with formation of an *iso*quinazindolone (III). The

(III.)





(IV.)

application of this process to 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (IV) (Manske and Robinson, this vol., p. 240) resulted in the production of rutæcarpine. The identity of the synthetical specimen with one of natural origin was proved by careful direct comparison.

Experimental.

iso*Quinazindol-2-one* (III).—A mixture of phthalimidine (6·7 g.), methyl anthranilate (8 g.), and phosphorus trichloride (30 g.) was heated under reflux for 3 hours, the product was decomposed by ice and hydrochloric acid, and the *base*, precipitated by addition of alkali to the solution, filtered after treatment with charcoal, was purified to some extent by redissolution in hydrochloric acid and recovery. It crystallised from ethyl alcohol in slender, colourless needles (yield, 4 g.), m. p. 205—206° (Found: C, 76·9; H, 4·5; N, 11·9. $C_{15}H_{10}ON_2$ requires C, 76·9; H, 4·3; N, 12·0%). This

* The degradative fission of rutæcarpine yields 3-β-aminoethylindole-2-carboxylic acid, and recently this acid has been reconverted into rutæcarpine. Its *o*-nitrobenzoyl derivative was reduced and then dehydrated. A brief account of the experiment will be found in the May (1927) issue of the *Journal of the Pharmaceutical Society of Japan*. Y. A.

weak base is soluble in moderately concentrated hydrochloric acid and is sparingly soluble in most neutral organic solvents.

Rutœcarpine (II).—A mixture of the ketotetrahydrocarboline (4 g.), methyl anthranilate (5 g.), and phosphorus trichloride (20 g.) was heated under reflux for 4 hours and the excess of the trichloride was then removed by distillation under diminished pressure. The residue was decomposed with ice, the solid collected and boiled with concentrated hydrochloric acid (200 c.c.), and the solution filtered hot. Unchanged lactam was recovered from the solution; the insoluble, pale brown residue crystallised from boiling ethyl alcohol in colourless needles (yield about 1·5 g.), m. p. 257—258° (Found: C, 75·3; H, 4·7; N, 14·7. Calc. for $C_{18}H_{13}ON_3$: C, 75·2; H, 4·5; N, 14·6%), which also melted at 257—258° when mixed with a specimen of rutæcarpine from *Evodia rutœcarpa*. The experiments involved in the following observations were carried out side by side with both specimens and with identical results in every case. The substance is sparingly soluble in most organic solvents and crystallises from ethyl acetate in characteristic, very slender needles; it is very stable and may be distilled in small quantities in a high vacuum without decomposition. The bright yellow solution in sulphuric acid becomes deep brown on the addition of Mandelin's reagent or colourless on dilution with water. On boiling with dilute hydrochloric acid, the substance does not dissolve but is coloured yellow. The colourless solution in acetic acid exhibits a bluish-green fluorescence after the introduction of a few drops of sulphuric acid. The hot alcoholic solution becomes yellow on the addition of solid potassium hydroxide, but after dilution with water the colour is discharged and the unchanged substance separates in needles, m. p. 257°.

THE UNIVERSITIES OF TOKYO
AND MANCHESTER.

[*Received, June 1st*, 1927.]

CCXXI.—*Experiments on the Synthesis of Anthocyanins. Part III.*

By ALEXANDER ROBERTSON and ROBERT ROBINSON.

THE fact that we have investigated 4'-, 3-, and 7-glucosidoxyflavylium salts (Parts I and II), which, unlike the anthocyanins, are not derivatives of phloroglucinol, is partly due to our having attacked the problem of the synthesis of the naturally occurring pigments in stages, but partly also to the circumstance that the methods employed in the anthocyanidin syntheses have been found in some details to be inapplicable to related glucosides.

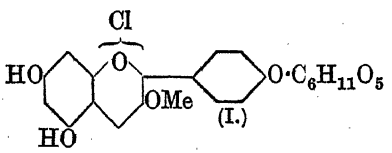
In the preparation of the latter, the condensation has hitherto been effected in dry ethereal solution and under these conditions *O*-triacetylphloroglucinaldehyde does not react satisfactorily with the appropriate ketones. In order to overcome this difficulty, it was necessary to obtain mono- or di-acetylated phloroglucinaldehydes, but all efforts to prepare the monoacetyl or monocarbomethoxy-derivatives failed. On the other hand, O-*diacetylphloroglucinaldehyde* was found to be the product when a solution of phloroglucinaldehyde in aqueous sodium hydroxide was agitated with an ethereal solution of acetic anhydride. No clear proof of the constitution of this substance can be adduced, but it must be either diacetoxysalicylaldehyde or diacetoxy-*p*-hydroxybenzaldehyde and the reaction with ferric chloride is in agreement with the former hypothesis.

This view is supported by the observation that the substance condenses readily with ω-methoxyacetoveratrone in ethereal solution in presence of hydrogen chloride, with ultimate production of cyanidin trimethyl ether, whereas *O*-triacetylphloroglucinaldehyde cannot be employed in flavylium salt syntheses in ethereal solution. This aldehyde exhibits some tendency to condense with suitable components under the requisite conditions to glucosidoxyflavylium salts, but the yields are very unsatisfactory. It was then found that O-*monobenzoylphloroglucinaldehyde* could be prepared by the Schotten–Baumann method, and this substance not only answered our immediate purpose, but also proved to be by far the best form in which to introduce phloroglucinaldehyde in all syntheses leading to pyrylium salts of anthocyanidin type.

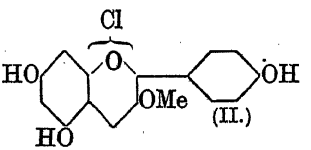
The results of anthocyanidin syntheses which depend in the final stages on demethylation by means of hydriodic acid are subject to unexplained variations and uniformity cannot be relied upon. Partial demethylation is a frequent occurrence, and is not only capricious in its incidence, but is also difficult to detect by analysis; in other cases, Zeisel and Herzig–Meyer determinations of the product may prove the absence of methoxyl and yet the experiment has gone awry, since the material, usually quite crystalline, does not exhibit the normal reactions. We suspect the influence of inorganic catalysts in promoting nuclear methylation by a process analogous to Claisen's transformation of phenyl allyl ether to allylphenol. In view of this uncertainty, we are engaged in the repetition of the anthocyanidin syntheses by processes not involving demethylation. Employing *O*-benzoylphloroglucinaldehyde, we have already obtained benzoylpelargonidin and cyanidin chlorides. We do not wish to imply that demethylation of methoxylated flavylium salts by means of hydriodic acid is always an unsatisfactory

process, since in many cases it gives excellent results, and we are often compelled to rely upon this effective but clumsy method.

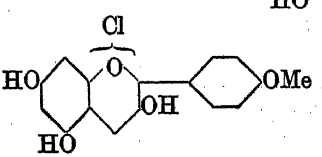
Experiments bearing on the constitution of *O*-benzoylphloroglucinaldehyde are in progress; it is either 2-benzoyloxy-4 : 6-dihydroxybenzaldehyde or 4-benzoyloxy-2 : 6-dihydroxybenzaldehyde. The benzoyloxyflavylium salts obtained with the aid of this aldehyde are stable towards acids, but are hydrolysed by alkalis, and the hydroxyflavylium salts are then recoverable by the action of acids on the product. The condensation of *O*-benzoylphloroglucinaldehyde with *p-O*-tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone (Part I, J., 1926, 1717) in ethereal solution with the aid of hydrogen chloride yielded an intermediate which was hydrolysed by means of methyl-alcoholic ammonia and subsequent treatment with hydrochloric acid with formation of a *pelargonidin methyl ether glucoside chloride* (I). This substance closely resembles a natural monoglucosidic anthocyanin in general character.



(I.)



(II.)



(III.)

The related sugar-free flavylium salt (II) derived on hydrolysis with 15% hydrochloric acid was synthesised independently, and furthermore the isomeride (III) has been obtained for comparison. The colour reactions of these pelargonidin chloride methyl ethers with sodium carbonate differ in a characteristic manner and a consideration of them shows (*a*) that callistephin and other anthocyanins derived from pelargonidin are certainly not 4′-glucosides, callistephin being probably a 3-glucoside (the position 5 is excluded on account of the fact that alcoholic solutions of callistephin, unlike those of pelargonenin, do not exhibit fluorescence. It is probable, although not yet quite certain, that position 7 can be excluded for the same reason), and (*b*) that partial demethylation of pelargonidin chloride 3 : 4′-dimethyl ether with hydriodic acid yields the 4′-monomethyl ether (III).

EXPERIMENTAL.

O-Diacetylphloroglucinaldehyde.—A mixture of pure phloroglucinaldehyde (6 g.), dissolved in *N*-sodium hydroxide (54 c.c.), and

ether (150 c.c.) was cooled to — 5°, and acetic anhydride (12 c.c.) gradually added with vigorous shaking. The reaction proceeded rapidly. The ethereal layer was separated, and the aqueous solution twice extracted with fresh ether. The combined ethereal solutions were mixed with water (10—15 c.c.), the ether was distilled, and the residue washed repeatedly with cold water. The oil gradually crystallised in contact with water and after a few days was ground, allowed to remain under water for 2 days longer, and then collected (5·5 g.). The solution of this product in 80% alcohol, after treatment with charcoal, deposited crystals on slow evaporation; these recrystallised from 60% alcohol (charcoal) in almost colourless, prismatic needles, m. p. 102—103°, presenting a homogeneous appearance under the microscope (Found: C, 55·4; H, 4·3. $C_{11}H_{10}O_6$ requires C, 55·5; H, 4·2%). The substance is readily soluble in ether and moderately readily soluble in cold methyl or ethyl alcohol. An alcoholic solution develops a wine-red coloration on the addition of ferric chloride. On further acetylation by means of acetic anhydride and potassium carbonate, an almost theoretical yield of *O*-triacetylphloroglucinaldehyde was obtained. The product had m. p. 156—157°, whereas Pratt and Robinson (J., 1925, **127**, 1182) give m. p. 151°. A specimen prepared from phloroglucinaldehyde, however, after repeated crystallisation from ethyl alcohol and then from methyl alcohol, sintered at 151° and had m. p. 156—157°. A mixture of the two specimens had m. p. 156—157°. Attempts to prepare monoacetylphloroglucinaldehyde by limiting the amount of acetic anhydride employed gave mixtures of the above diacetyl derivative and unchanged phloroglucinaldehyde. No definite carbomethoxy-derivatives could be obtained. Treatment of alkaline solutions of phloroglucinaldehyde at 0° with methyl chloroformate resulted in the immediate deposition of a brick-red product.

O-*Benzoylphloroglucinaldehyde.*—The phloroglucinaldehyde employed in the preparation of this substance should be obtained by the use of freshly distilled anhydrous hydrogen cyanide, since the material resulting from the modification described by Pratt and Robinson (J., 1925, **127**, 1132) is difficult to free from a colouring matter which has a deleterious effect on the yield. Phloroglucinaldehyde (5·2 g.) was added to a solution (cooled to 10°) of potassium hydroxide (1·7 g.) in water (150 c.c.). The mixture was cooled to — 5°; part of the potassium derivative then separated in glistening plates. Benzoyl chloride (2·35 g.) was then introduced in three portions with very vigorous shaking, which was continued until the odour of the chloride had almost disappeared. The mixture was stirred for ½ hour with an excess of aqueous sodium bicarbonate,

and the solid was then collected, washed, again triturated with aqueous sodium bicarbonate, isolated, and dried in the air (yield, 7·5 g.). The crude product was dissolved in hot alcohol (100 c.c., charcoal), and the filtered solution poured into water (400 c.c.). The emulsion quickly resolved itself into a suspension of hair-fine needles, which were isolated (5 g.) and found to be sufficiently pure for many purposes. The substance crystallises from chloroform (charcoal) in colourless, elongated prisms which become pink at 155°, darken at 185°, turn brick-red at 195°, and melt at 198—200° to a dark red liquid (Found: C, 64·8; H, 3·8. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%). The substance is easily soluble in ether and the simple alcohols, moderately readily soluble in hot chloroform, and very sparingly soluble in carbon tetrachloride. It gives a wine-red coloration with ferric chloride in alcoholic solution.

4′-β-*Glucosidoxy*-5 : 7-*dihydroxy*-3-*methoxyflavylium Chloride* (I).—A cold solution of *O*-benzoylphloroglucinaldehyde (0·6 g.) and *p*-*O*-tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone (0·5 g.) in dry ether (100 c.c.) was slowly saturated with hydrogen chloride; it gradually assumed a deep orange-red colour and then exhibited a strong yellowish-green fluorescence. A part of the product crystallised, and after 4 days the remainder was precipitated by the addition of ether (100 c.c.). The isolated salt (0·5—0·7 g.) dissolved in alcohol to an intensely fluorescent solution, but it could not be recrystallised, because pseudo-base formation occurred in solutions containing less than 5—6% of hydrochloric acid, and the use of more concentrated acid solutions caused hydrolysis. A solution of the crude product (2·7 g.), from several experiments, in methyl alcohol (200 c.c.) was saturated at 0° with ammonia and allowed to remain at 0° for 24 hours. The ammonia and methyl alcohol having been removed in a vacuum in the cold, the residue crystallised from 75% methyl alcohol containing 3% of hydrogen chloride in masses of microscopic, prismatic needles (1·2 g.) (deposition slow). The salt was then dissolved in 4% aqueous hydrochloric acid at 60—70° and separated on cooling in red, prismatic needles which showed a weak golden reflex only after being dried in a vacuum (Found in air-dried material: C, 47·7; H, 5·7. Found in material dried over soda-lime in a vacuum for 24 hours: C, 53·1; H, 5·3. $C_{22}H_{23}O_{10}Cl,4H_2O$ requires C, 47·6; H, 5·7%. $C_{22}H_{23}O_{10}Cl,H_2O$ requires C, 52·8; H, 5·0%. The monohydrate is very hygroscopic). When heated in a capillary tube, the salt evolves steam above 100°, sinters at 125°, and darkens and melts at 130—131°. The glucoside is easily soluble in cold 0·5—2% hydrochloric acid and in cold 50% methyl alcohol containing 4% of hydrogen chloride; it is easily soluble in hot aqueous hydrochloric acid (up to 20%).

The aqueous acid solutions are not completely extracted on being shaken with *iso*amyl alcohol. The alcoholic hydrochloric acid solutions are deep red, dilute aqueous solutions are orange-red, and in all cases the solutions are not fluorescent. The sodium carbonate reaction is dark wine-red, becoming dirty brown, whilst the addition of sodium acetate to an acid solution produces a more stable, intense dark red coloration. The *picrate* separated from a hot 80% alcoholic solution of the salt containing an excess of picric acid in compact, deep red, spherical masses of microscopic crystals. It darkens at 125°, is almost black at 170°, and melts with further decomposition at 186—188°.

5 : 7 : 4′-*Trihydroxy*-3-*methoxyflavylium Chloride* (II).—(A). A slow stream of hydrogen chloride was passed through a solution of *p*-hydroxy-ω-methoxyacetophenone (Part I, *loc. cit.*) (1·6 g.) and *O*-triacetylphloroglucinaldehyde (2·8 g.) in anhydrous formic acid (10 c.c.) for 4 hours, and the mixture kept for 36 hours. The salt precipitated by ether was collected (3 g.) and hydrolysed by boiling aqueous alcoholic hydrochloric acid during 5 minutes; on cooling, a red, amorphous material was deposited. This was extracted by boiling water, and 20% hydrochloric acid was added to the filtrate until a faint turbidity appeared. On cooling, the salt separated in stellate aggregates of dark red, prismatic needles. Recrystallisation from 3—4% hydrochloric acid gave freely twinning, elongated, nearly rectangular, microscopic prisms which were dark red in mass and crimson by transmitted light under the microscope (Found in material dried over soda–lime for 12 hours: C, 56·6; H, 4·6. $C_{10}H_{15}O_5Cl,H_2O$ requires C, 56·7; H, 4·4%). When crystallised from a mixture of hydrochloric acid and ethyl alcohol, highly characteristic, boat-shaped, microscopic plates are obtained. These have a reddish-brown colour and a greenish reflex, but this is lost on exposure to air. This salt is sparingly soluble in cold dilute hydrochloric acid (down to 0·5%) and is only moderately readily soluble in hot hydrochloric acid; very dilute solutions have a brownish orange-red colour, hot concentrated aqueous solutions and alcoholic solutions are crimson, and all solutions are non-fluorescent. Aqueous sodium carbonate dissolves the salt, giving a stable, intense, reddish-violet solution, more bluish-violet in thin layers. Willstätter and Burdick (*Annalen*, 1916, **412**, 162) state that "Die säure Losung des Callistephins schlägt mit Soda und sogar mit Alkalilauge nur in Rotviolett bis Violettrot um, während Pelargonenin schon mit Soda violett blau wird." In this connexion, it is interesting to note that 3 : 7 : 4′-trihydroxyflavylium chloride gives a definitely bluer alkali colour-reaction than the 3 : 5 : 7-trihydroxymethoxyflavylium chloride. In alcoholic solution, for

example, the former, like pelargonenin, gives a pure blue coloration (compare Willstätter and Bolton, *Annalen*, 1916, **412**, 136; Pratt and Robinson, J., 1923, **123**, 193). *iso*Amyl alcohol extracts the salt completely from an aqueous acid solution. Pseudo-base formation was observed.

(B). Characteristic, twinning, rectangular prisms separated in the course of 2 minutes when the above-described glucosidoxydihydroxymethoxyflavylium chloride was boiled in 15% aqueous hydrochloric acid solution. The substance was recrystallised and identified by its reactions, solubility relations, and crystalline form with the pelargonidin chloride 3-methyl ether prepared as in (A) above. The filtrate from this hydrolysis was extracted with *iso*amyl alcohol in order to remove the last traces of flavylium chloride and with ether to remove the *iso*amyl alcohol; it was then found to reduce Fehling's solution.

3 : 5 : 7-*Trihydroxy*-4'-*methoxyflavylium Chloride* (III).—A solution of anisoylcarbinol (0·6 g.) (Tiffeneau, *Compt. rend.*, 1910, **150**, 1182) and *O*-triacetylphloroglucinaldehyde (1 g.) in formic acid (15 c.c.) was saturated with hydrogen chloride and after 36 hours the product was precipitated by ether and collected. It was dissolved in alcohol (200 c.c.) and concentrated hydrochloric acid (20 c.c.), the solution boiled for 5 minutes, the greater part of the alcohol removed by distillation, and the salt precipitated by the addition of concentrated hydrochloric acid. Separation from accompanying red impurities was effected by extraction with boiling 0·5% hydrochloric acid, the acid concentration of the filtrates was increased to 8—10%, and finally the substance was crystallised from 2% hydrochloric acid, separating in crimson, microscopic, rhombic prisms (Found in material dried over soda-lime for 12 hours: C, 56·4; H, 4·6. $C_{16}H_{13}O_5Cl,H_2O$ requires C, 56·7; H, 4·4%). The yield, as in the similar synthesis of peonidin, was poor and we have since found that *O*-benzoylphloroglucinaldehyde gives much better results than the triacetate in condensations with benzoylcarbinol derivatives. In mass this salt has a dark brown colour and exhibits a weak bluish-green reflex. When it is crystallised from aqueous-alcoholic hydrochloric acid (about 5%), highly characteristic, regular, diamond-shaped plates are obtained. The salt is very sparingly soluble in cold aqueous hydrochloric acid and not readily soluble even in boiling 2% hydrochloric acid. Concentrated aqueous solutions are crimson, very dilute solutions are brownish orange-red; alcoholic solutions are bluish eosin-red. The reaction with sodium carbonate is characteristic, the solutions, both alcoholic and aqueous, being strongly dichroic, red in thick layers and bluish-purple in thin layers. Under

some conditions of illumination, the liquid appears green and violet. The specimen of incompletely demethylated pelargonidin chloride dimethyl ether described as crystallising in diamond-shaped plates (Pratt and Robinson, J., 1925, **127**, 1188) has been re-examined and undoubtedly contains a large proportion of the monomethyl ether now described. The crystal forms are identical and the colour reactions with sodium carbonate are closely similar. The dichroism observed in both cases was identical, but the specimen from the demethylation gave a slightly more bluish-purple colour in thin layers and probably contains a little pelargonidin chloride.

The authors wish to thank the Royal Society and the Chemical Society for grants which have defrayed a part of the cost of the investigation.

THE UNIVERSITY OF MANCHESTER. [*Received, June 7th*, 1927.]

CCXXII.—*A New Form of Thermostat and Observation Tubes for Polarimetric Work.*

By THOMAS STEWART PATTERSON.

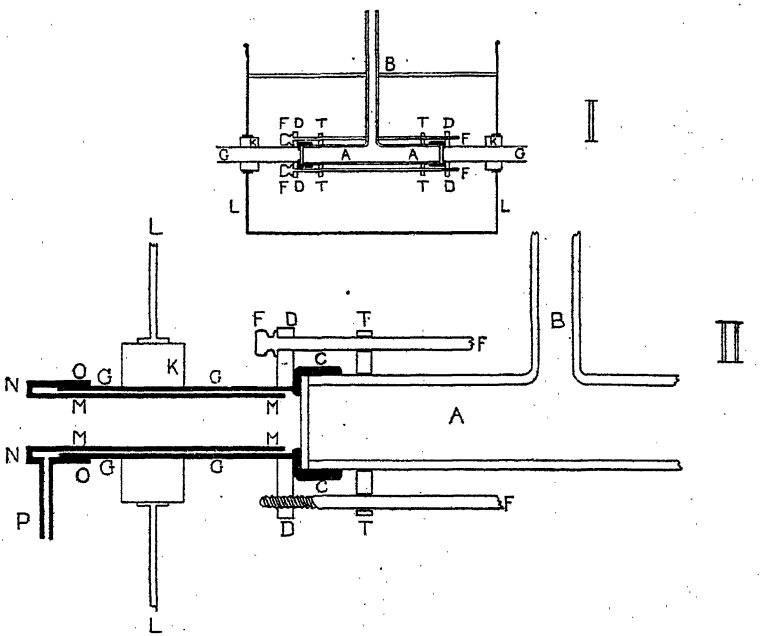
IN polarimetric investigation, it is of very great importance to maintain a steady known temperature while the rotation of the active substance is being observed. The author in the course of his work has tried various forms of apparatus designed for this purpose, and some fifteen years ago adopted one which, since it has been found to give accurate results and to be easy to manipulate, may be of use to others engaged in similar work.

The polarimeter tube is so placed as to be in direct contact with the water in the thermostat. The upper part, I, of the accompanying figure gives a general idea of the whole apparatus. The polarimeter tube, A, has attached to it a side tube, B, reaching above the level of the liquid in the thermostat. The glass end discs may be cemented to the polarimeter tube or may be fixed in position by means of pieces of rubber tubing marked C in the lower, more detailed part of the figure. These act partly to prevent ingress of water into the tube or exit of material from it, and serve also, by being turned over the end of the cover glass, as washers to take up the pressure exerted by the brass end pieces, DD, of which there is one at each end. These are fastened together by means of the brass rods, FF, which have a small knob at one end and a screw at the other; the latter fits into a corresponding screw in one of the discs. These are really arranged as in the upper sketch, but the lower sketch shows the

details of each end. These rods just pass easily through holes in two collars, T T, which thus serve to keep the end plates, D D, in position. To the flanges, D D, are brazed brass tubes, G G. When the apparatus is in use, these brass tubes are passed through rubber bungs which fit into collars in the wall, L, of the bath, as shown at K K.

In carrying out an observation, the thermostat is emptied of liquid, and the polarimeter tube in its support of flanges and rods, either filled with the active liquid or empty, is introduced through the rubber bungs to appear as shown in I, an operation easily

FIG. 1.



performed. The active liquid may now be introduced into the tube, if this has not already been done, and the thermostat filled with water, upon which, preferably, there should float a layer of oil.

The temperature of the thermostat may be controlled by any suitable form of adjustable thermo-regulator, that used in this laboratory being one designed by the author (*J. Soc. Chem. Ind.*, 1902, **21**, 456). The liquid in the thermostat is also, in most cases, mechanically stirred, but this is not necessary for temperatures of 0°, 100°, and that of the atmosphere. By means of suitable screws on the legs of a quadrupod or tripod stand, the thermostat is adjusted so that the axis of the tube coincides accurately with the axis of the polarimeter.

Owing to the fact that there is direct contact between the glass of the polarimeter tube and the water in the thermostat, the temperature in the polarimeter tube becomes constant very rapidly; and since, between observations, the water in the thermostat may be replaced by water which, previously, has been heated very near the desired temperature, the time which must be allowed to elapse before a new temperature is established is reduced to a minimum. The variation of the temperature during the time required for the observations is very small indeed and the temperature may be maintained within about one-tenth of a degree of any desired value for long periods.

The temperature of boiling water is very easy to adjust too, especially when a layer of oil is used. A very small flame is sufficient to keep the water in the thermostat in ebullition and the temperature in the polarimeter tube is then exceedingly steady.

This is the upper limit of temperature at which we have used the apparatus, but it would not be difficult to adapt it for higher temperatures, by using concentrated potassium carbonate solution, for example, instead of water. For temperatures above 100°, we use an oil thermostat with an air chamber in which the tube is heated.

The apparatus described, however, may be used for temperatures *below* that of the atmosphere and it is possible to obtain very constant readings at a temperature of zero, which again is, of course, a very simple one to obtain; the thermostat is filled with a slush of ground ice and water. The difficulty then arises, however, that moisture is apt to condense on the end plates of the polarimeter tubes. To get over this difficulty, various methods were tried, but ultimately one which is exceedingly effective and also very simple has been adopted. This is illustrated in II. A piece of brass tubing, M M M M, which fits into the tube G G with a clearance of, perhaps, half a millimetre, and of a length sufficient to reach to about a millimetre or two from the end plate of the polarimeter tube, is soldered by an annulus, N, to another short piece of brass tube, O O, which just slips on to the outside of the tube G G. To this tube, O, is soldered a short narrow brass tube, P. The whole part M N O P can thus easily be removed when not wanted and equally easily replaced in position when required; one such part is fitted at each end of the polarimeter tube. The little tubes P are then connected to two of the arms of a Y piece, the third arm of which, in turn, connects with a drying tower containing sulphuric acid and pumice stone, this again being connected to a gas holder containing air. When observations are to be made at a temperature below that of the atmosphere, a quite slow current of dry air is

duced through the tubes P passes through the narrow space between the tubes M M and G G to near the end plate of the polarimeter tube, and out through the tube M M M M. The air close to the polarimeter end plate is thus kept thoroughly dry and no moisture is deposited upon the end plate. This arrangement is surprisingly efficient and even when a freezing mixture of carbon dioxide and alcohol is used as cooling agent, which causes the whole of the apparatus quickly to be covered with ice, a perfectly clear view through the polarimeter tube may be obtained, so long as the current of air is passing.

This little piece of apparatus will be found of very considerable value, since by its means it is easy to determine rotation values at zero, which is probably the most suitable standard temperature for the expression of polarimetric results, inasmuch as it can always be easily obtained, but which hitherto has been avoided, doubtless owing to the difficulty occasioned by the condensation of moisture on the end discs.

The bath which we use is 25 cm. long by 5 broad by 17 deep and accommodates comfortably tubes 160 mm. in length.

UNIVERSITY OF GLASGOW. [*Received, June 2nd,* 1927.]

CCXXIII.—*Some Substituted Phenyl Styryl Ketones, with Remarks on the Condensation of Cinnamic Acid with Resorcinol and Pyrogallol.*

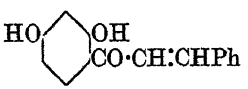
By THOMAS ERIC ELLISON.

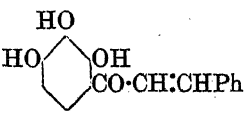
THE condensation of benzoic acid with resorcinol in presence of zinc chloride takes place in two stages; 2 : 4-dihydroxybenzophenone is formed first and then, by further heating and participation of a second molecule of resorcinol in the reaction, 3-hydroxy-9-phenylfluorone. Pyrogallol behaves in an analogous fashion to resorcinol.

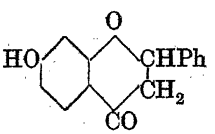
The behaviour of other simple carboxylic acids with these two phenols depends essentially on the relative velocity of the second stage of the reaction. When this is slow, as, *e.g.*, with acetic acid, the hydroxy-ketone can readily be isolated: when it is rapid, the only products that can be obtained are fluorones or more complex colouring matters. In the case of cinnamic acid, the primary condensation products would be hydroxyphenyl styryl ketones (hydroxychalkones); and the formation of chalkones in this way has actually been reported, that of 2 : 4-dihydroxyphenyl styryl ketone (I) from cinnamic acid and resorcinol by Bargellini

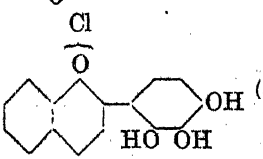
and Marantonio (*Atti R. Accad. Lincei*, 1908, **17**, ii, 119) and that of 2 : 3 : 4-trihydroxyphenyl styryl ketone (II) from cinnamic acid and pyrogallol by Dutta and Watson (J., 1912, **101**, 1238).

In the hope of being able to extend this method to the synthesis of some of the less accessible chalkones, their work has now been repeated, but the compounds in question were obtained neither by following the details given by the authors nor by any variations of the method, the only substances isolated being more complex colouring matters. To throw more light on the question, the chalkones (I) and (II) have been synthesised by more orthodox methods, and it is found that they are not identical with the substances held to be chalkones by the authors cited. It seems, therefore, that if, in the condensation of cinnamic acid with resorcinol and pyrogallol by means of zinc chloride, chalkones are formed at all, which is very probable, they are so rapidly transformed into more complex products that it is impossible to isolate them.

(I.) 


(II.)

(III.) 


(IV.)

Resacetophenone and benzaldehyde condense together in alkaline-alcoholic solution to give a mixture of 2 : 4-dihydroxyphenyl styryl ketone (I) and the isomeric 7-hydroxyflavanone (III). It is not uncommon to find chalkone and flavanone being simultaneously formed by this method, and the possibility of the two products being, in this particular case, geometrical isomerides is excluded by the colourless nature of the second substance and the fact that it yields only a monoacetyl derivative. Gallacetophenone and benzaldehyde condense together readily both in acid and in alkaline solution. By boiling with alcoholic hydrochloric acid, they yield benzylidenebisgallacetophenone, $C_6H_5\cdot CH[CH_2\cdot CO\cdot C_6H_2(OH)_3]_2$ (Kostanecki and Blumstein, *Ber.*, 1900, **33**, 1478). The same compound is obtained by saturating a solution of the reagents in glacial acetic acid with dry hydrogen chloride.

Despite the quantitative nature of this reaction, similar compounds cannot be obtained when benzaldehyde is replaced by anisaldehyde, salicylaldehyde, piperonal, or *m*-nitrobenzaldehyde. By the use of alcoholic potash, the required chalkone (II) is obtained

in good yield. In order to establish the generality of the last-mentioned method, which does not appear to have been applied hitherto to gallacetophenone, the benzaldehyde was replaced in turn by salicylaldehyde, *m*-hydroxybenzaldehyde, vanillin, and resorcylaldehyde. The last two were found not to condense appreciably with gallacetophenone under the action of alcoholic potash, whereas salicylaldehyde gave a moderate yield of 2 : 3 : 4-trihydroxyphenyl 2-hydroxystyryl ketone,

$$C_6H_2(HO)_3{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH,$$

and *m*-hydroxybenzaldehyde a small amount of 2 : 3 : 4-trihydroxyphenyl 3-hydroxystyryl ketone. Salicylidenegallacetophenone is very slowly converted into 2′ : 3′ : 4′-trihydroxy-2-phenylbenzopyrylium chloride (IV) by the action of anhydrous hydrogen chloride on the suspension in ether; but owing to the small amount of this substance which has so far been isolated, the investigation of it is not yet completed.

EXPERIMENTAL.

2 : 4-*Dihydroxyphenyl Styryl Ketone* (I) and 7-*Hydroxyflavanone* (III).—To a solution of resacetophenone (20 g.) and benzaldehyde (13·3 g.) in methyl alcohol (120 c.c.), potassium hydroxide (40 g. in 40 c.c. of water) was added and the mixture was kept at 65° for 3½ hours and then poured into water. Unchanged benzaldehyde having been extracted with ether, an excess of hydrochloric acid was added, which precipitated a yellow oil (about 12 g.). After 12 hours, the partly solidified oil was carefully treated with glacial acetic acid, and the undissolved solid, consisting of almost pure 7-hydroxyflavanone, was crystallised from toluene. Addition of water to the acetic acid solution precipitated a mixture of the chalkone and flavanone, which were ultimately separated by a tedious fractional crystallisation from toluene, in which the chalkone is the more soluble. 7-*Hydroxyflavanone* crystallises from toluene in colourless needles, m. p. 189° (Found: C, 74·8; H, 5·3. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). It is insoluble in water and moderately easily soluble in alcohol or glacial acetic acid. In cold sodium carbonate solution, it gives a colourless solution which turns yellow on boiling. In sodium hydroxide, it at once forms a yellow solution which goes darker on heating owing to the conversion of the flavanone into the chalkone, but the change is never complete.

The flavanone (1 g.) was heated on the water-bath for 3 hours with acetic anhydride (10 c.c.) and anhydrous sodium acetate (5 g.). The *acetyl* derivative thus produced crystallised from 50% alcohol

in colourless needles, m. p. 98° (Found: C, 72·0; H, 5·0. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

2 : 4-*Dihydroxyphenyl styryl ketone* crystallises from toluene in bright yellow, rectangular prisms, m. p. 133—134° (Found: C, 74·9; H, 5·3. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). It is very slightly soluble in boiling water and very soluble in alcohol, glacial acetic acid, and acetone. It forms a deep yellow solution in concentrated sulphuric acid.

2 : 3 : 4-*Trihydroxyphenyl Styryl Ketone* (II).—Gallacetophenone (4·2 g.) and benzaldehyde (2·7 g.) were dissolved in alcohol (4·5 c.c.), and potassium hydroxide (9 g. in 10 c.c. of water) was added. The mixture was kept at 60° for 3 hours and then poured into dilute hydrochloric acid, on which the *chalkone* separated as a brown oil (about 4 g.) which slowly solidified. It was repeatedly crystallised from 75% methyl alcohol, animal charcoal being used to remove a slightly fluorescent, dark impurity, and was thus obtained in orange-yellow prisms containing methyl alcohol of crystallisation. After drying at 110°, it had m. p. 165—166° (Found: C, 70·2; H, 4·9. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%). It forms deep brown solutions in alkali and in concentrated sulphuric acid. It is practically insoluble in water, slightly soluble in benzene and toluene, and very soluble in acetic acid and alcohol.

2 : 3 : 4-*Trihydroxyphenyl* 2-*Hydroxystyryl Ketone*.—Gallacetophenone (4·2 g.) and salicylaldehyde (3·1 g.), dissolved in alcohol, were treated with potassium hydroxide (10 g. in 10 c.c. of water), and the solution kept at 65° for 3½ hours. Dilute hydrochloric acid was then added which precipitated the *chalkone* (3·3 g.) as a brown oil, which soon solidified. It crystallised from 75% methyl alcohol in long, yellow needles having a light brown colour in bulk. It became almost black at 205° and melted with complete decomposition at 224—225° (Found: C, 65·8; H, 4·4. $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%). The chalkone is insoluble in water, benzene, and chloroform, slightly soluble in boiling xylene, and very soluble in acetone and alcohol. It gives dark brown solutions in alkali and in concentrated sulphuric acid, and on heating with concentrated hydrochloric acid it is slowly converted into the pyrylium chloride, but with much decomposition.

2 : 3 : 4-*Trihydroxyphenyl* 3-*Hydroxystyryl Ketone*.—Gallacetophenone (2·5 g.), *m*-hydroxybenzaldehyde (1·8 g.), potassium hydroxide (5 g. in 5 c.c. of water), and alcohol (40 c.c.) were heated together at 75° for 8 hours. Addition of dilute hydrochloric acid precipitated the *chalkone* (1 g.), which crystallised from 80% methyl alcohol (charcoal) in bright yellow needles, melting at 219—220° to a dark red liquid (Found: C, 66·0; H, 4·7. $C_{15}H_{12}O_5$ requires

C, 66·2; H, 4·4%). It forms a deep brown solution in alkali and a deep orange solution in concentrated sulphuric acid.

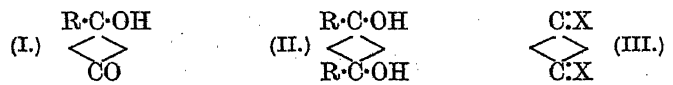
The author is indebted to Mr. A. Russell, B.Sc., for his valuable assistance with the experimental work.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST. [*Received, May 23rd*, 1927.]

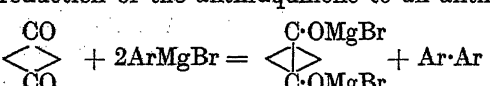
CCXXIV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part II.*

By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and JOHN LAURENCE WILTSHIRE.

THE action of Grignard solutions upon anthraquinone, 2-methylanthraquinone, and alizarin dimethyl ether has been studied by Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 797), Guyot and Staehling (*ibid.*, 1905, **33**, 1104), Haller and Comptesse (*Compt. rend.*, 1910, **150**, 1290), Guyot and Vallette (*Ann. Chim.*, 1911, **23**, 363), Padova (*ibid.*, 1910, **19**, 353), Kovaché (*ibid.*, 1918, **10**, 226), Sirker (J., 1915, **107**, 1242), Clarke and Carleton (*Ber.*, 1908, **41**, 935; *J. Amer. Chem. Soc.*, 1911, **33**, 1966), and Ingold and Marshall (J., 1926, 3080) and has been found to lead to the alkyl- or aryl-hydroxyanthrone (I) or the dialkyl- or diaryl-dihydroanthraquinol (II), the last class of compound being by far the most readily accessible.

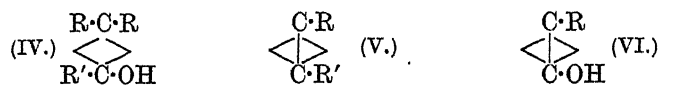


These last are stable towards alkaline reducing agents, although very easily reduced to the anthracene derivatives in acid solution, but when R is an alkyl group there is usually a marked tendency for loss of water to take place with the production of an alkylideneanthracene (III) or a polymerisation product of this. The yields of diol (II) recorded in different experiments are very varied. For example, by the action of magnesium phenyl bromide on anthraquinone, Haller and Guyot obtained only a 10% yield of the diol, Ingold and Marshall a 34% yield, and Kovaché an 80% yield. It has now been found that one of the chief reasons for the poor yields frequently obtained lies in the reducing action of the Grignard solution, which leads to the partial reduction of the anthraquinone to an anthraquinol:



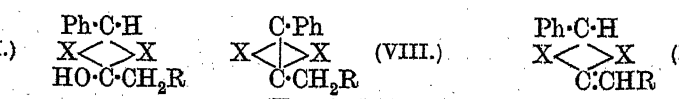
a reaction which is somewhat analogous to a pinacol condensation, but which takes place in the complete absence of metallic magnesium (compare Boyd and Hatt, this vol., p. 898). Occasionally the reduction proceeds further and a considerable quantity of the diarylanthracene may be formed.

The action of Grignard solutions on anthrones has been studied by Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 797), Guyot and Staehling (*ibid.*, 1905, **33**, 1104, 1144), Jüngermann (*Ber.*, 1905, **38**, 2868), Krollpfeiffer and Branscheid (*ibid.*, 1923, **56**, 1617), Sieglitz and Marx (*ibid.*, 1923, **56**, 1619), Kehrmann, Monnier, and Ramm (*ibid.*, 1923, **56**, 169), Barnett and Matthews (*ibid.*, 1926, **59**, 1429), and Barnett, Cook, and Matthews (*ibid.*, 1926, **59**, 2863) and has been found to lead to a dihydroanthranol (IV), from which (when R = H) loss of water takes place extremely easily (for example, by treatment with an acid) with the formation of an alkyl- or aryl-anthracene (V).



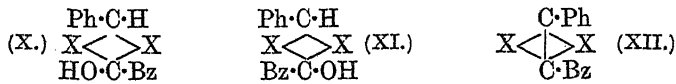
When neither R group represents a hydrogen atom the yields of the dihydroanthranol are excellent, although in this case the subsequent loss of water is impossible, but when one of these groups is a hydrogen atom the Grignard solution brings about considerable conversion of the anthrone into the enolic anthranol (VI) and poorer yields of the dihydroanthranol are obtained. The reaction is also complicated in some cases by reduction taking place which is probably due, at least in part, to loss of an alcohol from the dihydroanthranol first formed (compare Branscheid, *Dissert.*, Marburg, 1923). The method is, nevertheless, an extremely valuable one for the synthesis of both *meso*-alkyl- and *meso*-aryl-anthracenes, although of less general application than might be expected.

The action of magnesium alkyl halides on 1 : 5-dichloro-9-phenyl-anthrone gave oily products (probably VII) from which in some cases yellow and fluorescent (VIII) and/or colourless and non-fluorescent (IX) isomeric substances were obtained.



The action of magnesium benzyl chloride on 1 : 5-dichloro-9-phenylanthrone yielded a dihydroanthranol to which the *trans*-configuration is assigned (X), since it could not be converted into phenylbenzyldichloroanthracene (XII), all attempts at dehydration

leading either to the isolation of the unchanged material or to the production of indefinite substances from which no pure product could be isolated. A less amount of the *cis*-dihydroanthranol (XI) must have been formed simultaneously, as the liquors from the *trans*-isomeride gave, on evaporation, an oil from which phenylbenzyldichloroanthracene (XII) was easily obtained as a yellow, fluorescent substance by treatment with acids:



The fact that phenyldichloroanthrone can yield alkylidene compounds whereas phenylanthrone yields only the anthracene derivatives is in harmony with previous observations on the stabilising influence of α-chlorine atoms on the derivatives of 9 : 10-dihydroanthracene, and the inter-conversion of the alkylidene compounds (IX) and the anthracene derivatives (VIII) would supply definite proof of the theory of transannular tautomerism (Barnett, Cook, and Matthews, *loc. cit.*). To this end a detailed examination of the products described in the present communication is now in progress.

Ingold and Marshall (*loc. cit.*) have shown that the 9 : 10-diarylanthracenes undergo a reversible deepening in colour when heated with an inert solvent of high boiling point and have attributed this to dissociation of the " bridge " bond leaving the *meso*-carbon atoms in the tervalent state. Liebermann, Glawe, and Lindenbaum (*Ber.*, 1904, **37**, 3337) and Schlenk (*Annalen*, 1912, **394**, 191) have previously brought forward evidence of the existence of anthracene derivatives in which one of the *meso*-carbon atoms is tervalent, although the latter observer was unable to detect dissociation of 9 : 10-diphenylanthracene. The present authors have confirmed qualitatively Ingold and Marshall's statements as regards the reversible deepening in colour of the diarylanthracenes in mesitylene solution, and have found that not only the diarylanthracenes mentioned in the sequel, but also the 9-phenyl-10-alkylanthracenes exhibit the same phenomenon. A similar remark applies to 9-phenylanthracene, although in this case the effect is so slight as to be barely perceptible. The colourless products to which the alkylidene formula (IX) has been attributed in the foregoing do not become coloured when their solutions in mesitylene are boiled, and this is regarded as additional evidence in favour of the structure assigned to them.

Ingold and Marshall assume, by analogy with the hexa-arylethanes, that the formation of disodio- and dipotassio-compounds of the diarylanthracenes indicates the existence of a dissociable " bridge " bond. This argument is inadmissible, as anthracene

itself gives similar compounds (Schlenk, Appenrodt, Michael, and Thal, *Ber.*, 1914, **47**, 473) and, indeed, the formation of these compounds is merely a further example of the resemblance of the " bridge " to an ethylenic bond.

In any case, the dissociation of the diaryl- and arylalkyl-anthracenes is just as much in harmony with the orthoquinonoid formula as with the " bridge " formula and there appears to be no method of differentiating between these two structures. Arguments based on physical properties such as refractivity (compare Auwers, *Ber.*, 1920, **53**, 941) are fictitious, since the " bridge," if it does exist, does not behave like an ordinary single bond, although represented as such. In all its chemical properties it exactly resembles an ethylenic bond and in calculating a physical constant it should be treated as a double bond. If this is done, the " bridge " and the orthoquinonoid structures represent each a system containing seven double bonds and are therefore indistinguishable. The chief advantages of the " bridge " formula are that it represents reactions of transannular addition and loss somewhat more clearly than the orthoquinonoid formula does, and it does not predict the existence of two α- or two β-monosubstitution products which would be expected from the orthoquinoid structure in the absence of a conception of dynamic equilibrium. For these reasons, it is used in this communication and is regarded as the best symbolical representation of the anthracene molecule whether the " bridge " bond has any real existence or not.

EXPERIMENTAL.

9 : 10-*Diphenyl*-9 : 10-*dihydroanthraquinol* was prepared from anthraquinone and magnesium phenyl bromide in 50% yield without using the special precautions recommended by Kovaché. The pure product melted at 260—263° (Haller and Guyot give 247° and Ingold and Marshall 252—254°). To prove the formation of anthraquinol, the crude Grignard product was poured on ice and ammonium chloride, the ether removed by distillation in steam, and the resulting solid extracted with boiling dilute sodium hydroxide solution, all these operations being performed in an inert atmosphere. When air was blown through the deep red alkaline extract, anthraquinone was deposited, and after recrystallisation it was identified by the method of mixed melting points.

In another experiment in which the crude diol was recrystallised from xylene, 9 : 10-diphenylanthracene was isolated from the liquors and identified by direct comparison with an authentic sample.

9 : 10-Di-*p*-anisyl-9 : 10-dihydroanthraquinol * was prepared by

* This compound was previously prepared by Haller and Comptesse (*loc. cit.*), who also reduced it to dianisylanthracene.

Ingold and Marshall's method (*loc. cit.*) from anthraquinone and magnesium *p*-anisyl bromide.* The inherent improbability of their statement that octahydrodiphenylanthracene is obtained when this diol is heated with hydriodic acid and phosphorus at 150° led us to repeat the experiment and we have identified their product as 9 : 10-dihydroanthracene by direct comparison with an authentic sample. A previous example of facile loss of a *meso*-group on heating with hydriodic acid has been given by one of us (J., 1926, 1684).

1-*Chloro*-9 :10-*diphenylanthracene*.—By boiling 1-chloroanthraquinone for 4 hours with 4 mols. of an ethereal solution of magnesium phenyl bromide a crude product was obtained from which 1-chloro-9 : 10-diphenylanthracene was isolated by recrystallisation first from toluene and then from acetic acid. It then formed a yellow, crystalline powder, m. p. 185° (Found: Cl, 9·7. $C_{26}H_{17}Cl$ requires Cl, 9·7%). In addition to the above, the crude product also contained 1-chloroanthraquinone (due to atmospheric oxidation of the anthraquinol) and as it gave an indigo-blue colour with concentrated sulphuric acid the diol also was doubtless present. For the preparation of 1-chloro-9 : 10-diphenylanthracene, it was found best to remove the anthraquinone by extraction with alkaline hydrosulphite solution and then to reduce by boiling with zinc dust and acetic acid.

2-Chloro-9 : 10-diphenylanthracene was obtained as a yellow, crystalline powder, m. p. 194°, by reduction of the crude diol obtained from 2-chloroanthraquinone and magnesium phenyl bromide (Found: Cl, 9·7. Calc.: Cl, 9·7%). Subsequent to our preparation of this compound, it was described by Ingold and Marshall (*loc. cit.*).

1 : 5-*Dichloro*-9 : 10-*diphenyl*-9 : 10-*dihydroanthraquinol*.—A vigorous reaction took place when 12 g. of 1 : 5-dichloroanthraquinone were added to a cold ethereal solution of magnesium phenyl bromide (4 mols.). After boiling for 6 hours, the whole was poured on ice and solid ammonium chloride, and volatile substances were removed by distillation with steam. The crude product contained much dichloroanthraquinone (due to atmospheric oxidation of the anthraquinol) and this was removed by repeated extraction with large volumes of boiling alkaline hydrosulphite solution. The residue, recrystallised from nitrobenzene and from xylene, formed a colourless, crystalline powder which melted to a red liquid at

* 49 G. of pure *p*-bromoanisole were obtained when a solution of 52 g. of *p*-bromophenol in 200 c.c. of 10% potassium hydroxide solution was heated on the water-bath until neutral (about 2 hours) with 70 g. of methyl *p*-toluenesulphonate, the whole being shaken from time to time. After addition of a large excess of alkali and heating for an hour to destroy the excess of the ester, the bromoanisole was removed by distillation with steam, dried in ethereal solution with calcium chloride, and distilled.

320° and gave an indigo-blue solution in concentrated sulphuric acid. The yield was 5 g. and numerous attempts under various conditions failed to improve it (Found: C, 71·9; H, 4·45. $C_{26}H_{18}O_2Cl_2$ requires C, 72·0; H, 4·2%). Unlike all other dihydroanthraquinols which have been studied up to the present, the above diol is extremely stable to reduction, and prolonged boiling with zinc dust and acetic acid, with or without the addition of hydrochloric acid, failed to convert it into diphenyldichloroanthracene.

1 : 5 : 9 : 10-*Tetrachloro*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene* was obtained when dry hydrogen chloride was passed through a solution of the above diol in boiling tetralin, and also when 1 : 5-dichloro-9 : 10-diphenylanthracene was treated with a solution of chlorine in carbon tetrachloride. It formed colourless crystals which melted to a red liquid at 250° and liberated iodine from potassium iodide in acetic acid solution (Found: Cl, 30·3. $C_{26}H_{16}Cl_4$ requires Cl, 30·2%).

9-*Benzylanthracene*.—By the action of a well-cooled solution of magnesium benzyl chloride (3 mols.) on anthrone (1 mol.) there was obtained a colourless, crystalline compound, m. p. 50°. This dihydroanthranol (IV. R = H; R′ = C_7H_7) is less stable than its isomeride (Cook, J., 1926, 2160) and passes into 9-benzylanthracene on keeping over-night in a vacuum desiccator.

Neither *o*-tolyl- nor *p*-anisyl-anthracene could be obtained from anthrone by the action of magnesium tolyl or anisyl bromide, most of the anthrone being recovered unchanged.

Action of Grignard Solutions on 9-Phenylanthrone.—In all cases, 9 g. of finely powdered 9-phenylanthrone were added to an ethereal solution of the Grignard reagent (3 mols.), the whole being cooled in a freezing mixture. After remaining over-night at the ordinary temperature, the mixture was poured on ice and solid ammonium chloride, the ethereal layer washed, and the ether removed by distillation. The residual crude dihydroanthranol passed very easily into the alkylanthracene by heating with acetic acid alone or with the addition of acetic anhydride or a few drops of hydrochloric or dilute sulphuric acid. In order to establish the reaction, the dihydroanthranol was purified and analysed in three cases. Attempts to effect dehydration in such a way that an alkylidene derivative was formed were not successful. When the reaction was carried out with magnesium *iso*butyl bromide, only 9-phenylanthracene was obtained, a result which may be due to the reducing properties of the Grignard solution but is more probably to be attributed to loss of butyl alcohol from the crude dihydroanthranol. The same result was obtained when the Grignard solution was carefully freed from metallic magnesium.

9-Phenyl-10-α-naphthyldihydroanthranol was found to be more stable than the other dihydroanthranols, but it was converted into 9-phenyl-10-α-naphthylanthracene by boiling for 3 hours with acetic anhydride.

Phenyl-*n*-butylanthracene, phenylbenzylanthracene, and phenyl-α-naphthylanthracene are yellow in colour, but all the other hydrocarbons are colourless. They are all strongly fluorescent. The dihydroanthranols are all colourless and non-fluorescent.

The following table gives the m. p. and analytical figures for carbon and hydrogen, the calculated values being in brackets. The solvent from which final crystallisation was effected is given after the m. p.

Group.	Phenylalkyl (or aryl)-dihydroanthranol.	Phenylalkyl (or aryl)-anthracene.
Et	—	M. p. 110° (alcohol). 93·4, 6·5 ($C_{22}H_{18}$: 93·6, 6·4%).
Pr$^{\alpha}$	M. p. 148—150° (much lower in a preheated bath) (benzene–light petroleum). 87·6, 7·2 ($C_{23}H_{22}O$: 87·9, 7·0%).	M. p. 115—116° (alcohol). 93·1, 6·7 ($C_{23}H_{20}$: 93·2, 6·75%).
Pr$^{\beta}$	—	M. p. 166—167° (methyl ethyl ketone–alcohol). 93·2, 6·9 ($C_{23}H_{20}$: 93·25, 6·75%).
Bu$^{\alpha}$	—	M. p. 156° (ethyl acetate). 92·6, 7·1 ($C_{24}H_{22}$: 92·9, 7·1%).
*iso*Amyl	—	M. p. 203—204° (benzene–alcohol). 92·3, 7·45 ($C_{25}H_{24}$: 92·6, 7·4%).
Bz	M. p. 177° (benzene). 89·3, 6·2 ($C_{27}H_{22}O$: 89·5, 6·1%).	M. p. 155° (acetic acid). 94·0, 6·0 ($C_{27}H_{20}$: 94·2, 5·8%).
α-$C_{10}H_7$	M. p. 260—262° (toluene). 90·2, 5·65 ($C_{30}H_{22}O$: 90·4, 5·5%).	M. p. 244—245°* (benzene–alcohol). 94·5, 5·4 (Calc.: 94·7, 5·3%).

* Previously made by a different method by Guyot and Staehling (*Bull. Soc. chim.*, 1905, **33**, 1120), who gave the m. p. as 229°.

Action of Grignard Solutions on 1 : 5-*Dichloro*-9-*phenylanthrone.*—In all cases the reaction was carried out by adding finely powdered 1 : 5-dichloro-9-phenylanthrone (m. p. 254° and not 245° as erroneously given previously; Barnett and Matthews, *Ber.*, 1926, **59**, 670) to an ethereal solution of 3—4 mols. of the Grignard reagent, the whole being cooled in a freezing mixture. After remaining over-night at the ordinary temperature, the mixture was poured on ice and solid ammonium chloride. The washed and filtered ethereal solution was then evaporated to dryness. Under these conditions viscous oils which could not be made to crystallise were obtained with all the magnesium alkyl halides, and these were

therefore dissolved in acetic acid and heated on the water-bath with the addition of a little sulphuric or hydrochloric acid.

1 : 5-*Dichloro*-9-*phenyl*-10-*methylene*-9 : 10-*dihydroanthracene* (IX; R = H), after recrystallisation from ethyl acetate, formed a snow-white, crystalline powder which showed no fluorescence; m. p. 150° (Found : C, 74·6; H, 4·5; Cl, 20·8. $C_{21}H_{14}Cl_2$ requires C, 74·8; H, 4·2; Cl, 21·1%).

1 : 5-*Dichloro*-9-*phenyl*-10-*ethylidene*-9 : 10-*dihydroanthracene* (IX; R = Me). The crude dihydroanthranol, when boiled with acetic acid and a mineral acid, gave chiefly a red, resinous product, but by dissolving this in ethyl acetate, adding alcohol, and then allowing the solution to evaporate slowly at the ordinary temperature, a colourless product (about 0·5 g. from 7 g. of phenyldichloroanthrone) was obtained which, after recrystallisation from alcohol and then from ethyl acetate, melted at 159° (Found : C, 75·3; H, 4·9. $C_{22}H_{16}Cl_2$ requires C, 75·2; H, 4·6%).

n-*Propyl derivatives.* By treating the red resin obtained by heating the crude dihydroanthranol with acetic and hydrochloric acids as described above, a small amount of a colourless, non-fluorescent product was isolated which, after recrystallisation from methyl alcohol, melted at 135°. This was undoubtedly 1 : 5-*dichloro*-9-*phenyl*-10-*propylidene*-9 : 10-*dihydroanthracene* (IX; R = Et) (Found : C, 75·3; H, 5·1. $C_{23}H_{18}Cl_2$ requires C, 75·6; H, 4·9%).

In another experiment, in which the crude dihydroanthranol was treated with acetic and sulphuric acids, the red resin, when treated as described above, yielded a small amount of a yellow, strongly fluorescent substance which, after being washed with boiling methyl alcohol and recrystallised from ethyl acetate, melted at 196°. This product was almost certainly 1 : 5-*dichloro*-9-*phenyl*-10-n-*propyl-anthracene* (VIII; R = Et), but the yield was less than 0·1 g. from 7 g. of phenyldichloroanthrone (Found : C, 75·8; H, 5·6. $C_{23}H_{18}Cl_2$ requires C, 75·6; H, 4·9%).

iso*Propyl derivative.* Treatment of the crude dihydroanthranol with acetic and either sulphuric or hydrochloric acids yielded a red resin from which, by treatment with ethyl acetate as described above, about 0·2 g. of a yellow, strongly fluorescent, crystalline powder, m. p. 195° (to a red liquid), was isolated which analysis indicated to be 1 : 5-*dichloro*-9-*phenyl*-10-iso*propylanthracene* (Found : C, 75·0; H, 5·1. $C_{23}H_{18}Cl_2$ requires C, 75·6; H, 4·9%).

n- *and* iso-*Butyl derivatives.* In neither case was it found possible to isolate sufficient pure material from the red resin for analysis, but from the *n*-butyl product a minute amount of a yellow, fluorescent, crystalline powder, m. p. 186° (to a red liquid), was obtained.

1 : 5-*Dichloro*-9-*phenyl*-10-*benzyl*-9 : 10-*dihydroanthranol* (X).—The reaction between phenyldichloroanthrone and magnesium benzyl chloride was carried out as with other magnesium alkyl halides. After the mixture had been poured on ice and ammonium chloride, the colourless solid which was insoluble in ether was collected, washed with ether, and recrystallised from alcohol; m. p. 173° (yield, 3·5 g. from 7 g. of phenyldichloroanthrone) (Found: Cl, 16·5. $C_{27}H_{20}OCl_2$ requires Cl, 16·5%). This product was much more stable to acids than most dihydroanthranols; when boiled under reflux with glacial acetic acid and either hydrochloric or sulphuric acid, or with acetic anhydride, or when heated alone to 300°, it underwent some change, but repeated crystallisation of the product from various solvents failed to yield any substance of constant melting point.

1 : 5-*Dichloro*-9-*phenyl*-10-*benzylanthracene* (XII).—When the ethereal solution from the above preparation was evaporated to dryness, an oil was left which rapidly passed into a crystalline solid when heated on the water-bath with glacial acetic acid containing a little hydrochloric acid. After boiling with animal charcoal in acetone–aqueous alcohol solution and recrystallisation from benzene, this was obtained as a yellow, crystalline powder, m. p. 209°. The solution showed a strong blue fluorescence (Found: C, 78·4; H, 4·8. $C_{27}H_{18}Cl_2$ requires C, 78·4; H, 4·6%).

1 : 5-*Dichloro*-9 : 10-*diphenyl*-9 : 10-*dihydroanthranol* was obtained in good yield from phenyldichloroanthrone and magnesium phenyl bromide and after recrystallisation from alcohol melted and evolved gas at 201° (Found: Cl, 17·2. $C_{26}H_{18}OCl_2$ requires Cl, 17·0%).

Attempts to prepare the corresponding α-naphthyl compound led only to the isolation of unchanged phenyldichloroanthrone.

1 : 5-*Dichloro*-9 : 10-*diphenylanthracene*.—The above dihydroanthranol was boiled with glacial acetic acid containing a little hydrochloric acid, and the product recrystallised several times from amyl alcohol and from benzene–light petroleum. It then formed a yellow, crystalline powder, m. p. 236° after previous sintering (Found: Cl, 17·9. $C_{26}H_{16}Cl_2$ requires Cl, 17·8%). On oxidation with sodium dichromate in boiling glacial acetic acid, it passed into the same dihydroanthraquinol that was obtained by the action of magnesium phenyl bromide on 1 : 5-dichloroanthraquinone.

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SIR JOHN CASS TECHNICAL INSTITUTE,
JEWRY STREET, E.C. 3.

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CCXXV.—*Studies of Dynamic Isomerism. Part XXIII. Mutarotation in Aqueous Alcohols.*

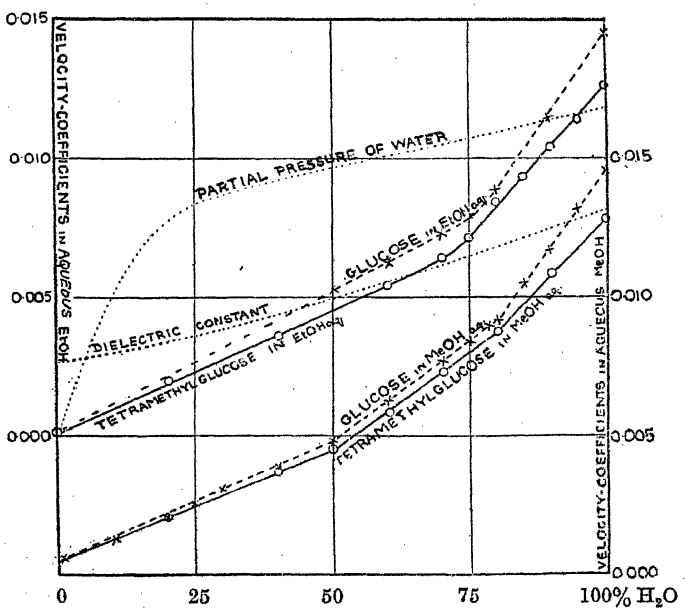
By Evan Matthew Richards, Irvine John Faulkner, and Thomas Martin Lowry.

The present paper summarises the mutarotation data for some 80 solutions of glucose and of tetramethyl glucose in aqueous methyl and ethyl alcohols. These measurements formed part of a research on the influence of water concentration on velocity of mutarotation, and may therefore be regarded as a sequel to a recent investigation of the velocity of mutarotation of tetramethyl glucose and tetra-acetyl glucose in aqueous acetone (Part XXI; J., 1926, 720). The results, however, were of an entirely different character from those recorded in the preceding papers of this series. Thus, whereas solutions in aqueous pyridine gave a curve with a strongly developed maximum (J., 1925, **127**, 2883), and those in aqueous acetone gave a drooping curve approaching asymptotically to the axis of concentration (J., 1926, 721), the curves for solutions in aqueous alcohols show an approximate proportionality between water concentratation and velocity, which persists up to 50% and up to about 70% of water in the case of methyl and ethyl alcohol, respectively.

It is not easy to give a precise interpretation of these facts. The direct proportionality between water content and velocity of mutarotation, which has been established by these present experiments, was regarded by Baker, Ingold, and Thorpe as a logical deduction from the hydrate theory of mutarotation, a conclusion that was illustrated by a diagram on which a line passing through the origin was labelled "Theoretical for Lowry and Armstrong's Mechanism" (J., 1924, **125**, 281). Since, however, the lines which represent the influence of water concentration on the velocity of mutarotation in the two aqueous alcohols do not point towards the value for pure water, but to a velocity which is only about two-thirds as great, we cannot adopt the elementary view that mutarotation depends on a simple mass action, in which the catalytic activity of the water is proportional to its volume concentration and independent of all other factors. Moreover, we have already shown in the case of aqueous acetone that the velocity of mutarotation is not proportional to the "fugacity" of the water, since the partial vapour pressure of this component rises steeply in the region of small concentrations, whereas the velocity curves rise only very slowly from a horizontal asymptote. A similar conclusion can now be drawn in reference to aqueous ethyl alcohol, since the steep rise in the partial vapour pressure of the water, recently recorded by

Dobson (J., 1925, **127**, 2872), is again in complete contrast with the slow progressive increase of velocity indicated by the straight lines of Fig. 1; nor does it appear likely that these unrelated curves could be brought into agreement by means of a correction based upon a hypothetical variation in the "fugacity" of the sugar. The new experimental evidence therefore provides ample confirmation of the view, which was already adopted in 1904 (J., **85**, 1567), that the velocity of mutarotation of the sugars in aqueous solutions is not controlled by the initial hydration of the anhydrous sugar (which

FIG. 1.



Mutarotation of glucose and tetramethyl glucose in aqueous methyl and ethyl alcohols.

can be regarded for this purpose as an instantaneous action) but by a much slower, and more fundamental, molecular rearrangement of the hydrate.

The factors which determine the velocity of this fundamental change of structure have not yet been fully disclosed. On general grounds it might be supposed that the velocity of the change would be proportional to the dielectric constant of the solution. The data for the dielectric constant of aqueous ethyl alcohol, which are plotted in Fig. 1, show that this property is related to the water content of the solutions according to a nearly linear law, which

extends (with a " sag " of 3 or 4 units in the centre of the curve) over the whole range of concentrations from 0 to 100%. Whilst, however, the dielectric constants for water and for ethyl alcohol are in the ratio 80 : 26 = 3 : 1, the velocities of mutarotation in the two solvents are in a ratio which cannot be less than 80 : 1, since the velocity coefficient for tetramethyl glucose falls from 0·0128 in water to a figure which is certainly less than 0·00016 in alcohol. The velocity of mutarotation in pure alcohol is indeed so small as to be almost negligible, whereas the dielectric constant of the medium is quite high enough to give to it the normal properties of an ionising solvent. Again, the curve showing the variation of the dielectric constant with the water content of the solution (like that which expresses the partial vapour pressure of the water) gives no indication whatever of the abrupt change of direction in the velocity curve, which is more than twice as steep for solutions containing from 75 to 100% H_2O as for solutions containing 0 to 70% H_2O.

Since none of these suggested relationships can be verified, the theory which links the velocity of mutarotation with the acid and basic properties of the medium (J., 1925, **127**, 1382) is at the present time the only one for which any experimental justification can be found. In the case of aqueous solutions, detailed evidence of this relationship is given by Euler's precise quantitative determination of the influence of hydrogen-ion concentration on the velocity of mutarotation of α- and β-glucose (*Z. anorg. Chem.*, 1925, **146**, 45; compare Hudson, *J. Amer. Chem. Soc.*, 1907, **29**, 1572, and Kuhn and Jacob, *Z. physikal. Chem.*, 1924, **113**, 389). In the case of solvents which are either wholly or partly non-aqueous, the hydrogen-ion concentrations are not known; but, since mutarotation can be arrested in media which possess only acid or only basic properties (as well as in media which possess neither), there can be little doubt that in these cases also the velocity of mutarotation must be a fairly simple function of these two properties.

Experimental.

The first experiments were made with samples of purified glucose and glucose hydrate supplied by Messrs. British Drug Houses, Limited. The suitability of these two samples for experiments on mutarotation was established by the fact that they gave normal values for the velocity coefficient in aqueous solutions, namely, $k_e = 0{\cdot}0146$ for the anhydrous sample and $k_e = 0{\cdot}0147$ for the hydrated sample at 20°.* We are indebted to Mr. G. F. Smith

* The values recorded here and in the preceding papers (Parts XIX to XXII) are for $k_e = 1/t\{\log_e(a_0 - a_\infty) - \log_e(a_t - a_\infty)\}$ and not for $k_{10} = 1/t\{\log_{10}(a_0 - a_\infty) - \log_{10}(a_t - a_\infty)\}$.

for a detailed investigation of this point. His observations showed that a commercial sample of glucose, which gave $k_e = [0{\cdot}0160]$, 0·0142, 0·0145, 0·0144 and 0·0144, after precipitation with alcohol gave $k_e = 0{\cdot}0153$, 0·0146. After crystallisation of the original sample from alcohol the product gave $k_e = 0{\cdot}0146$, 0·0146, whilst after a second crystallisation from alcohol it gave $k_e = 0{\cdot}0145$. The average, $k_e = \mathbf{0{\cdot}0146}$, of these very concordant data may be taken as a standard velocity coefficient in future tests of the purity of glucose. Values recorded by other workers are set out below for comparison.

Velocity of mutarotation of glucose in water.

	k_{10}.	k_e.	Observer.
(*a*) At 20°	0·0065	0·0150	Trey (*Z. physikal. Chem.*, 1895, **18**, 205).
	0·0059	0·0136	Parcus and Tollens (*Annalen*, 1890, **257**, 160).
	0·0061	0·0140	Levy (*Z. physikal. Chem.*, 1895, **17**, 307).
	0·00635	0·0146	Hudson and Dale (*J. Amer. Chem. Soc.*, 1917, **39**, 320).
	0·00627	0·0144	Mackenzie and Ghosh (*Proc. Roy. Soc. Edin.*, 1914, **35**, 22).
(*b*) At 25°	0·0104	0·0239	Osaka (*Z. physikal. Chem.*, 1900, **35**, 702).
	0·0074	0·0170	Trey (*ibid.*, 1897, **22**, 427).
	0·0100	0·0230	J. Meyer (*ibid.*, 1908, **62**, 59).
	0·0106	0·0244	Hudson (*J. Amer. Chem. Soc.*, 1907, **29**, 1573).
	0·0103	0·0237	Böeseken (*Ber.*, 1913, **46**, 2626).
	0·0104	0·0239	Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 387).
	0·0095	0·0219	Worley and Andrews (*J. Physical Chem.*, 1927, **31**, 744).

When dissolved in methyl alcohol (purified as described in Part XIX and containing about 99·5% MeOH), the anhydrous glucose gave a velocity coefficient $k_e = 0{\cdot}0006$. The corresponding value for tetramethyl glucose in a sample of methyl alcohol containing 99·1% MeOH was 0·0004, but this was subsequently reduced to 0·0002 by further purification of the alcohol, and even lower values have since been recorded by Worley and Andrews (*J. Physical Chem.*, 1927, **31**, 742) for the velocity coefficient of glucose in anhydrous methyl alcohol. The minimum velocity, however, represents a standard of purity which cannot be maintained in practice, since it corresponds with the conditions required to produce a complete arrest of mutarotation in a hydrocarbon solvent; Worley's velocities, as well as our own, are therefore a little too high at the alcohol end, but not to such an extent as to affect the general form of the velocity curves.

On account of the limited solubility of glucose in ethyl alcohol, suitable solutions could not be prepared in the higher ranges of concentration, and, even when methyl alcohol was used, it was

found convenient to prepare many of the solutions by filtering off an excess of the sugar, instead of by weighing out an exact percentage. Since identical velocity coefficients were obtained for these filtered solutions of glucose in 40% alcohol, and for solutions containing 4% of sugar, it appears that the velocity is not affected by the corresponding changes of sugar concentration; but, since filtration introduces an additional risk of contamination by catalytically active impurities, the difficulty of securing concordant velocities was increased considerably by the sparing solubility of the sugar, and in several cases the experiment had to be repeated more than once before a trustworthy minimum velocity could be recorded. It was therefore decided to regard all the data for glucose as preliminary determinations only, and to confirm the whole of the observations by duplicate experiments with tetramethyl glucose. This procedure had the double advantage that the sugar was of undoubted purity (compare J., 1925, **127**, 1387, footnote; 1926, 721), and that solutions of any desired strength could be prepared in an aqueous alcohol of any desired concentration and examined under comparable conditions. Moreover, it was found in practice that much less difficulty was experienced in securing consistent values for the velocity coefficients. Nevertheless, the complete concordance of the velocity curves for tetramethyl glucose with those already plotted for the parent sugar shows that the velocity coefficients finally recorded for glucose must have been substantially correct.

Results.—In order to economise space, all the direct readings of rotatory power have been omitted, but the unimolecular velocity coefficients deduced from them are set out in Tables I to IV below, and are represented graphically in Fig. 1. In general there is no great difference between the velocity of mutarotation in methyl and ethyl alcohols of a given water content, as is seen in the following summary of the data for glucose:

Water (%)	90	80	70	60	50	40	30	20	10
10,000 k_e (EtOH)	114	89	73	61	52	38	—	16	—
10,000 k_e (MeOH)	117	91	76	62	48	39	31	20	13

The two curves must cross, however, on either side of the 50% point, since the velocities at this concentration are slightly less in methyl than in ethyl alcohol, whereas they are slightly greater in the ranges outside 40 to 60% H_2O.

In Fig. 1, the full lines are for tetramethyl glucose, whilst the dotted lines refer to the less trustworthy experiments with glucose. Curves have also been added to show the dielectric constant, and the partial pressure of water vapour, in mixtures of ethyl alcohol and water. The experimental points have been represented as lying

TABLE I.

Mutarotation of Glucose in Aqueous Methyl Alcohol at 20°

Water %.	Sugar %.	Length of tube (cm.).	Vel. coeff., $k_e \times 10^4$.	Water %.	Sugar %.	Length of tube (cm.).	Vel. coeff. $k_e \times 10^4$.
100·0	5	20	146	60	5	20	63
95·2	3	,,	131	60	5	,,	62
90	5	,,	117	49·4	Sat.	60	48
,,	3	,,	118	49·2	3	20	48
85	,,	,,	105	40	1	60	39
82·6	,,	,,	100	30	1	,,	31
80·2	,,	,,	93	25·2	Sat.	,,	25
80·1	,,	,,	91	19·8	,,	,,	20
77·6	,,	,,	90	10	1	,,	13
75·3	,,	,,	84	1·5	Sat.	20	11
70·2	,,	,,	77	0·3	,,	60	8
70·0	5	,,	76	0·5	,,	,,	6

TABLE II.

Mutarotation of Glucose in Aqueous Ethyl Alcohol at 20°.

First series.			Second series.		
Water %.	Sugar %.	Vel. coeff., $k_e \times 10^4$.	Water %.	Sugar.	Vel. coeff., $k_e \times 10^4$.
100	5	146	74·7	Sat.	83
90	,,	114	,,	,,	83
80	,,	89	70·0	,,	72
70	,,	73	,,	,,	74
60	4	62	65·1	,,	70
,,	Sat.	63	,,	,,	68
50	,,	54	59·5	,,	61
			50·2	,,	52

TABLE III.

Mutarotation of Tetramethyl Glucose in Aqueous Methyl Alcohol at 20°.

Water %.	Sugar %.	Length of tube (cm.).	Vel. coeff., $k_e \times 10^4$.
100	5	20	127
,,	4	60	129
90·1	,,	,,	108
80·2	,,	,,	87
70·3	,,	,,	72
60·1	,,	,,	58
49·3	,,	,,	45
40·3	,,	,,	37
30·1	,,	,,	32
19·9	,,	,,	20
0·9	10	,,	4

TABLE IV.

Mutarotation of Tetramethyl Glucose in Aqueous Ethyl Alcohol at 20°.

Water %.	Sugar %.	Length of tube (cm.).	Vel. coeff., $k_e \times 10^4$.
100	5	20	127
95	,,	,,	114
90	,,	,,	104
85	,,	,,	93
80	,,	,,	84
75	,,	,,	71
70	,,	,,	61
60	,,	,,	54
40	,,	,,	36
20	,,	,,	20
0	,,	,,	2

on or near two straight lines for each of the series of observations in aqueous ethyl alcohol, and three straight lines in the case of methyl alcohol. It is probable that the points might be represented equally well as lying on a continuous curve, like Worley's data for

aqueous methyl alcohol at 25°; but for this purpose it would be essential that the curve should be indistinguishable from a straight line at concentrations up to 50% MeOH or 70% EtOH. Whilst, therefore, we do not suggest that there are any real " kinks " in the velocity curves, we have plotted the data on a linear framework, on the ground that they probably belong to the type, of which the real existence was demonstrated many years ago by Pickering (see especially *Phil. Mag.*, 1892, **33**, 134), which can be represented more closely by a pair of intersecting lines than by a single parabolic curve. Discontinuities of an even more striking character than those discovered by Pickering have been recorded by McCombie and his colleagues (J., 1921, **119**, 970; 1923, **123**, 2688) in the data for the velocity of saponification of esters in aqueous alcohols, where " breaks " were observed at 79, 64, 48, and 37% MeOH, and at 80, 62·5 or 59, 46, and 30% EtOH. Since their observations did not include the most dilute alcohols, it is not possible to make a direct comparison of these " breaks " with the rapid changes of curvature which are shown by our data at about 20% MeOH and 25% EtOH; but the change of curvature at 48 to 50% MeOH which is indicated by our data occurs at a concentration agreeing closely with that of their " break " at 48% MeOH. A " break " at this concentration has also been recorded in the viscosity, dielectric constant, and heat of dilution of this series of aqueous alcohols (McCombie, *loc. cit.*, p. 2690).

Summary.

(*a*) Data are given for the velocity of mutarotation of glucose and of tetramethyl glucose in aqueous methyl and ethyl alcohols.

(*b*) When the velocity coefficients are plotted against the water content of the solution, a linear relation is seen to extend up to about 50% H_2O in aqueous methyl alcohol and 70% H_2O in aqueous ethyl alcohol.

(*c*) No parallelism can be traced between the velocity of mutarotation and the partial pressure of the water, or the dielectric constant of the water–alcohol mixtures; but attention is directed to certain analogies with data recorded by McCombie and his colleagues for the velocity of saponification of esters dissolved in aqueous alcohols.

We are indebted to the Department of Scientific and Industrial Research for maintenance grants (to E.M.R. and I.J.F.) received during the period in which this research was carried out.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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CCXXVI.—*The Reimer–Tiemann Reaction with* m-*Chlorophenol.*

By HERBERT HENRY HODGSON and THOMAS ALFRED JENKINSON.

A MIXTURE of 4-chloro-2-hydroxy- and 2-chloro-4-hydroxy-benzaldehyde in almost equal quantities has been obtained from *m*-chlorophenol by the Reimer–Tiemann reaction. The constitutions of the two aldehydes were determined by converting the methyl ethers into the corresponding methoxy- and hydroxy-benzoic acids, and confirmed by preparing 4-chloro-2-methoxybenzaldehyde from 4-nitro-2-methoxytoluene and 2-chloro-4-hydroxybenzaldehyde from 2-chloro-4-nitrotoluene.

EXPERIMENTAL.

4-Chloro-2-hydroxy- and 2-Chloro-4-hydroxy-benzaldehyde.—An intimate mixture of slaked lime (140 g.), sodium carbonate (160 g.), *m*-chlorophenol (56 g.), water (1000 c.c.), and chloroform (104 g.) was submitted to the usual Reimer–Tiemann procedure. 4-Chloro-2-hydroxybenzaldehyde (13 g.) was removed by steam distillation, the operation being stopped when the much less volatile 2-chloro-4-hydroxybenzaldehyde began to pass over. The hot liquor in the flask was filtered from tar and, on cooling, deposited 2-chloro-4-hydroxybenzaldehyde (13 g.) in pale yellow, feathery needles.

With alcoholic potash in place of the lime–soda mixture, the reaction proceeded much more vigorously and produced more tar. Aqueous sodium and potassium hydroxides gave intermediate results.

4-Chloro-2-hydroxybenzaldehyde is very volatile in steam, being removed even from its yellow solutions in caustic alkalis. It is appreciably soluble in water and sulphurous acid, readily soluble in the usual organic solvents, and crystallises from alcohol or dilute acetic acid in long, colourless needles, m. p. 52·5° (Found: Cl, 22·6. $C_7H_5O_2Cl$ requires Cl, 22·7%). It has an odour resembling that of walnuts, gives a brown precipitate with ferric chloride, does not reduce ammoniacal silver nitrate or Fehling's solution, and is very resistant to acetylation and to oxidation by acid, neutral, or alkaline potassium permanganate. Although not readily methylated, yet it benzoylates easily under suitable conditions. In aqueous solution, it gives with copper and chromium sulphates, on careful treatment with dilute aqueous sodium hydroxide, a bright green *copper* salt and a dark green *chromium* salt. The *oxime* is fairly readily soluble in hot water, easily soluble in alkalis, alcohols, and glacial acetic acid, but less soluble in chloroform, and crystallises from alcohol in colourless

needles, m. p. 155° (Found: Cl, 20·8. $C_7H_6O_2NCl$ requires Cl, 20·7%). The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in orange needles, m. p. 257° (Found: Cl, 12·2. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%), and gives a dark cherry-red colour with aqueous sodium hydroxide. The *semicarbazone* is readily soluble in alkalis, moderately easily soluble in alcohol, and separates from glacial acetic acid in very pale yellow clusters of micro-crystals, m. p. 212° (Found: Cl, 16·8. $C_8H_8O_2N_3Cl$ requires Cl, 16·6%). The *benzoate* is best prepared by dissolving the aldehyde (0·6 g.) in ether (2 c.c.), adding pyridine (0·1 c.c.), and then a solution of benzoyl chloride (0·5 g.) in ether (2 c.c.); after vigorous shaking, removal of the ether, and extraction of the product with warm dilute hydrochloric acid, the white, waxy residue is washed with water and crystallised from alcohol, from which it separates in long, colourless needles, m. p. 98·5° (Found: Cl, 13·5. $C_{14}H_9O_3Cl$ requires Cl, 13·6%).

4-*Chloro*-2-*methoxybenzaldehyde* is obtained in only moderate yield by direct methylation. It has a faint sweet odour, is readily soluble in the usual organic solvents, and crystallises from alcohol in colourless needles, m. p. 74° (Found: Cl, 20·9. $C_8H_7O_2Cl$ requires Cl, 20·8%).

Alternative method of preparation. 4-Nitro-2-methoxytoluene (5 g.), dissolved in alcohol (20 c.c.), was added gradually to a hot solution of sodium hydroxide (3 g.) and sulphur (2 g.) in water (30 c.c.), and the mixture was heated for an hour on the water-bath. The alcohol and 2-methoxy-*p*-toluidine were then removed in steam, and the residue (2 g.) of crude 4-amino-2-methoxybenzaldehyde was dissolved in hot dilute sulphuric acid (30%), and converted by the Sandmeyer method into 4-chloro-2-methoxybenzaldehyde; after crystallisation from alcohol, this (Found: Cl, 20·7%), alone or mixed with the substance described above, melted at 74°.

The *oxime* crystallises from hot water in long, colourless needles, m. p. 132° (Found: Cl, 19·1. $C_8H_8O_2NCl$ requires Cl, 19·1%). The p-*nitrophenylhydrazone* separates from glacial acetic acid in bright orange clusters of micro-crystals, m. p. 238° (Found: N, 13·6. $C_{14}H_{12}O_3N_3Cl$ requires N, 13·7%), and develops with alkali a less intense but more violet colour than the unmethylated *p*-nitrophenylhydrazone. The *semicarbazone* crystallises from glacial acetic acid in very pale yellow, almost colourless micro-plates, m. p. 228° (Found: Cl, 15·5. $C_9H_{10}O_2N_3Cl$ requires Cl, 15·6%). 4-*Chloro*-2-*methoxybenzoic acid*, prepared by oxidising the aldehyde with aqueous alkaline potassium permanganate, crystallises from alcohol in clusters of micro-crystals, m. p. 148° (Found: Cl, 19·1.

$C_8H_7O_3Cl$ requires Cl, 19·0%). 4-Chloro-2-hydroxybenzoic acid was obtained by boiling the preceding acid with hydriodic acid (*d* 1·7); it was slowly volatile in steam, crystallised from water in fine, colourless needles which sublimed with slight decomposition at about 209° and melted at 211° (Varnholt, *J. pr. Chem.*, 1887, **36**, 27, gives m. p. 207°) (Found: Cl, 20·4. Calc.: Cl, 20·5%), and gave a reddish-violet colour with ferric chloride.

The 2-chloro-4-hydroxybenzaldehyde obtained as described above crystallised from mineral or glacial acetic acid in colourless needles, m. p. 147—148° (Gattermann, *Annalen*, 1907, **357**, 334, gives m. p. 146·5°) (Found: Cl, 22·6%). It does not react with ammoniacal silver nitrate or Fehling's solution, and gives only a slight precipitate with ferric chloride. The *copper* and *chromium* salts are of a lighter green colour than those of the 4-chloro-isomeride. The p-*nitrophenylhydrazone* crystallises from alcohol in dark red plates and from glacial acetic acid in vermilion-red clusters of micro-crystals, m. p. 288° (decomp.) (Found: Cl, 12·1. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%) and gives a bluer red with caustic alkalis than the 4-chloro-isomeride. The *semicarbazone* crystallises from alcohol in yellow clusters of micro-crystals, m. p. 214° (Found: Cl, 16·8. $C_8H_8O_2N_3Cl$ requires Cl, 16·6%), the *acetate* from dilute acetic acid in colourless needles, m. p. 51·5° (Found: Cl, 17·8. $C_9H_7O_3Cl$ requires Cl, 17·9%), and the *benzoate* from alcohol in colourless needles, m. p. 96·5° (Found: Cl, 13·6. $C_{14}H_9O_3Cl$ requires Cl, 13·6%).

2-Chloro-4-hydroxybenzaldehyde was also prepared, in almost quantitative yield, by treating 2-chloro-4-nitrotoluene with sodium hydroxide and sulphur (see above), diazotising the resulting amino-compound, and boiling the very stable diazo-compound with 40% sulphuric acid for 20 minutes.

The following derivatives were prepared in the same way as the corresponding 4-chloro-isomerides: The p-*nitrophenylhydrazone* separates from dilute acetic acid in orange-red needles, m. p. 249° (Found: N, 13·8. $C_{14}H_{12}O_3N_3Cl$ requires N, 13·7%), and gives a reddish-violet colour with aqueous-alcoholic alkali. The *semicarbazone* crystallises from alcohol in clusters of colourless micro-crystals, m. p. 240° (Found: Cl, 15·7. $C_9H_{10}O_2N_3Cl$ requires Cl, 15·6%). 2-*Chloro-4-hydroxybenzoic acid* crystallises from water (charcoal) in colourless needles, m. p. 159° (Found: Cl, 20·3. $C_7H_5O_3Cl$ requires Cl, 20·5%), and gives no definite colour with ferric chloride.

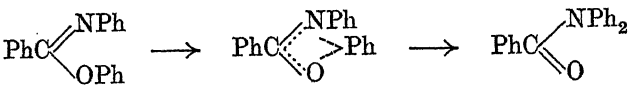
The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, April 30th*, 1927.]

CCXXVII.—*Imino-aryl Ethers. Part V. The Effect of Substitution on the Velocity of Molecular Rearrangement.*

By Arthur William Chapman.

In Part III (J., 1925, **127**, 1992), it was shown that *N*-phenylbenziminophenyl ether (I) could be completely converted into benzoyldiphenylamine (II) on heating. The change, which is unimolecular, was found to be best represented in terms of partial valencies (compare Robinson, *Mem. Manc. Lit. Phil. Soc.*, 1920, **64**, No. 4; Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379) thus :

(I.)  (II.)

When translated into the terms of the electronic theory, this formulation is ambiguous, since the migrating group may (*a*) carry with it both its shared electrons, (*b*) leave them behind, or (*c*) carry one and leave the other.

It seemed desirable to study the effect of replacing the migrating phenyl group in *N*-phenylbenziminophenyl ether by other groups, since according to (*a*) it would be expected that the relative attraction for electrons and the velocity of migration of different groups would follow the same order, but according to (*b*) the two values should be in the opposite order, whilst if (*c*) were correct the velocity of migration of a group should be independent of its attraction for electrons.

A number of *N*-phenylbenzimino-ethers, RO·CPh:NPh (III), having different groups (R) attached to the oxygen atom, were made and their velocities of rearrangement were compared. A special experiment showed that these changes were not appreciably reversible. It was found that the groups could be arranged in the following order of descending ease of migration : *o*-nitrophenyl > 2 : 4 : 6-trichlorophenyl > *p*-acetylphenyl > 2 : 4-dichlorophenyl > *o*-chlorophenyl > *m*-chlorophenyl > *p*-chlorophenyl and α- and β-naphthyls > phenyl and *o*-anisyl > *m*-anisyl > *p*-anisyl > methyl.

The velocities of migration of these groups are in the same order as the dissociation constants of the corresponding carboxylic acids and phenols ($R\cdot CO_2H$ and R·OH) and it must therefore be concluded that the mechanism of the isomeric change is represented by (*a*). Steric effects were evidently negligible, since the *o*-substituted compounds underwent rearrangement more rapidly than the corresponding *m*- and *p*-compounds.

Confirmatory evidence was then sought from the effect, on the

velocity of migration of a standard (phenyl) group, of variation of the groups attached to the nitrogen and carbon atoms. A number of *N*-substituted benziminophenyl ethers (IV) and *N*-phenylaryliminophenyl ethers (V) were accordingly prepared.

(IV.) PhO·CPh:NR PhO·CR:NPh (V.)

The greater the attraction of the group R for electrons in either (IV) or (V), the less readily will the oxygen atom release the electrons which bind it to the phenyl group, and hence, according to mechanism (*a*), the lower will be the velocity of rearrangement of the imino-ether.

This was indeed found to be the case, the ease of migration of the phenyl group being in the following order: *for various groups attached to the nitrogen atom* (*type* IV) *p*-anisyl>phenyl>*p*-chlorophenyl and α-naphthyl>*m*- and *o*-chlorophenyl and 2 : 4-dichlorophenyl>2 : 4 : 6-trichlorophenyl, *and for various groups attached to the carbon atom* (*type* V) *p*-anisyl>phenyl>*p*- and *o*-chlorophenyl>*p*-nitrophenyl and 2 : 4 : 6-trichlorophenyl.

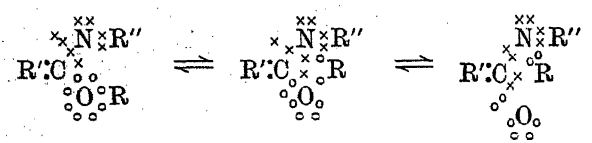
The isomeric change to a substituted amide which occurs when an imino-ether is heated at a sufficiently high temperature,

$$RO(\text{or } RS)\cdot CR'{:}NR'' \rightleftharpoons O(\text{or } S){:}CR'\cdot NRR'',$$

has now been studied in some detail (compare Part III, *loc. cit.*; Part IV, J., 1926, 2296). The rearrangement has been shown to be intramolecular and does not require any detectable amount of a catalyst. The behaviour of the imino-thioethers showed that, as might be expected, the change is reversible, but in the oxygen ethers equilibrium occurs so far over to the amide side that the reversibility is not appreciable.

The velocity of isomeric change varies greatly with the nature of the migrating group and of the groups attached to the carbon and nitrogen atoms. The greater the attraction of the migrating group for electrons (*i.e.*, the more "negative" it is) the greater the velocity of change, whilst negative groups attached to the carbon and nitrogen atoms retard the rearrangement.

These facts are readily explicable on the assumption that the migrating group carries over to the nitrogen atom the two covalency electrons by which it is bound to the oxygen atom, and the isomeric change can be expressed in symbolic form thus:



(where × represents an electron originally belonging to the nitrogen octet, and o one belonging to the oxygen octet).

The iminoether–amide rearrangement is a typical triad change, and it seems highly probable that the mechanism of a number of other such changes will be found to be explicable in similar terms.

EXPERIMENTAL.

The new imino-ethers required were prepared from the corresponding anilideiminochlorides and phenols by the method used for preparing *N*-phenylbenzimino-*m*-hydroxyphenyl ether (J., 1922, **121**, 1679). Unless otherwise stated, they were crystallised from alcohol, in which they were readily soluble when hot, but only sparingly soluble in the cold.

They were converted into the corresponding amides by heating at 280—310°, the products being purified by crystallisation from alcohol. Where possible, the amides thus obtained were compared directly with specimens prepared by other methods. The identity of two samples of a compound obtained from different sources was always confirmed by the method of mixed melting points.

N-*Phenylbenzimino*-m-*chlorophenyl ether* crystallised in colourless needles, m. p. 71° (Found : N, 4·6. $C_{19}H_{14}ONCl$ requires N, 4·55%). On heating, it was converted into benzoyl-*m*-chlorodiphenylamine (m. p. 101—102°; identical with an authentic specimen).

N-*Phenylbenzimino*-2 : 4-*dichlorophenyl ether*, pale yellow, slender prisms, m. p. 73—74° (Found : N, 4·2. $C_{19}H_{13}ONCl_2$ requires N, 4·1%).

N-*Phenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, colourless plates, m. p. 80—81° (Found : N, 3·95. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

N-*Phenylbenzimino*-o-*anisyl ether*, colourless, slender prisms, m. p. 113° (Found : N, 4·7. $C_{20}H_{17}O_2N$ requires N, 4·6%).

N-*Phenylbenzimino*-m-*anisyl ether* was obtained as a viscous oil which did not crystallise even after standing for 18 months (Found : N, 4·45%). The product of heating this imino-ether was also not obtained in crystalline form.

N-*Phenylbenzimino*-p-*anisyl ether*, colourless plates, m. p. 79—80° (Found : N, 4·8%).

N-*Phenylbenzimino*-p-*nitrophenyl ether*, pale yellow plates, m. p. 76—77° (Found : N, 8·9. $C_{19}H_{14}O_3N_2$ requires N, 8·8%). All attempts to cause this imino-ether to undergo isomeric change were unsuccessful. Decomposition with formation of tar occurred even at 150°.

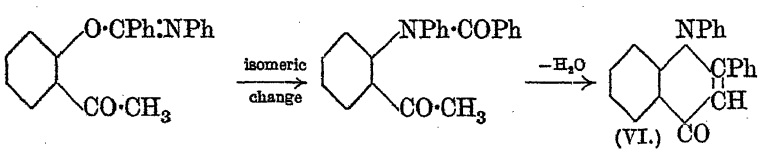
N-*Phenylbenzimino*-α-*naphthyl ether* crystallised from light petroleum in crusts, m. p. 89° (Found : N, 4·6. $C_{23}H_{17}ON$ requires

N, 4·3%). On heating, it gave benzoylphenyl-α-naphthylamine (m. p. 152°; identical with an authentic specimen).

N-*Phenylbenzimino*-β-*naphthyl ether* crystallised in thin leaflets from alcohol, in which it was only sparingly soluble at the boiling point; m. p. 127—128° (Found: N, 4·5%). It was hydrolysed by 50% sulphuric acid to β-naphthyl benzoate (m. p. 106—106·5°) and on heating gave benzoylphenyl-β-naphthylamine (m. p. 147°; identical with an authentic specimen).

N-*Phenylbenzimino*-p-*acetylphenyl ether*, m. p. 94—95° (Found: N, 4·6. $C_{21}H_{17}O_2N$ requires N, 4·45%).

N-*Phenylbenzimino*-o-*acetylphenyl ether*, m. p. 92—93° (Found: N, 4·6%). Instead of yielding benzoyl-*o*-acetyldiphenylamine when heated, it was converted into a basic compound, which crystallised from alcohol in thin leaves, m. p. 268°. The change was practically complete in 90 minutes at 267° (Found: C, 85·1; H, 5·1; N, 4·8; *M*, by Rast's micro-method, 285. $C_{21}H_{17}O_2N$ requires C, 80·0; H, 5·4; N, 4·45%; *M*, 315. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·1; N, 4·7%; *M*, 297). The loss of a molecule of water had evidently occurred and 1 : 2-*diphenyl*-4-*quinolone* (VI) was formed thus,



the second stage being analogous to the formation of 4-hydroxy-2-phenylquinoline from benzoyl-*o*-aminoacetophenone (Camps, *Arch. Pharm.*, 1901, **239**, 597).

N-o-*Chlorophenylbenziminophenyl ether*, prepared from *benz*-o-*chloroanilideiminochloride* (b. p. 204°/10 mm.) and phenol, crystallised in slender prisms, m. p. 65—66° (Found: N, 4·4. $C_{19}H_{14}ONCl$ requires N, 4·55%). On heating, it was converted into benzoyl-*o*-chlorodiphenylamine (m. p. 95°; identical with an authentic specimen).

N-m-*Chlorophenylbenziminophenyl ether*, prepared from *benz*-m-*chloroanilideiminochloride* (b. p. 211—213°/14 mm.), crystallised in rosettes of pale yellow, stout prisms, m. p. 66° (Found: N, 4·5%). It gave benzoyl-*m*-chlorodiphenylamine on heating (m. p. 100—101°; identical with an authentic specimen).

N-p-*Chlorophenylbenziminophenyl ether*, prepared from *benz*-p-*chloroanilideiminochloride* (b. p. 220—224°/20 mm.), formed stout prisms, m. p. 110° (Found: N, 4·4%). It yielded benzoyl-*p*-chlorodiphenylamine on heating (m. p. 110°; identical with an authentic specimen).

N-2 : 4-*Dichlorophenylbenziminophenyl ether*, stout prisms, m. p. 57—58° (Found : N, 4·0. $C_{19}H_{13}ONCl_2$ requires N, 4·1%). In this and several subsequent preparations the iminochloride was not distilled, but, after treatment of the anilide with phosphorus pentachloride and removal of the phosphorus oxychloride under reduced pressure on the water-bath, the residue was dissolved in dry ether and added directly to an alcoholic solution of sodium phenoxide.

N-2 : 4 : 6-*Trichlorophenylbenziminophenyl ether*, stout prisms, m. p. 88·5° (Found : N, 3·8. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

N-2 : 4 : 6-*Trichlorophenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, colourless needles, m. p. 141°, sparingly soluble in boiling alcohol (Found : N, 3·0. $C_{19}H_9ONCl_6$ requires N, 2·9%). Heated at 250—260° for 2 hours, it was mostly recovered unchanged, but at 280—300° *benzoyl*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexachlorodiphenylamine* (m. p. 194—195°. Found : N, 3·0%) was produced. The isomerisation of this imino-ether was therefore much slower than that of the corresponding *N*-phenylbenzimino-2 : 4 : 6-trichlorophenyl ether.

N-p-*Anisylbenziminophenyl ether*, prepared from *benz*-p-*anisidideiminochloride* (yellow flakes, m. p. 55°, b. p. 269—273°/162—180 mm. with some decomposition), formed yellow crystals, m. p. 100° (Found : N, 4·6. $C_{20}H_{17}O_2N$ requires N, 4·6%).

N-o-*Nitrophenylbenziminophenyl ether*, stout prisms, m. p. 67—68° (Found : N, 9·0. $C_{19}H_{14}O_3N_2$ requires N, 8·8%). Several unsuccessful attempts to cause rearrangement of this imino-ether were made. At 200—220°, it remained unchanged and above that temperature decomposed, giving much tar.

N-α-*Naphthylbenziminophenyl ether* formed a very viscous oil which would not crystallise (Found : N, 4·1. $C_{23}H_{17}ON$ requires N, 4·3%). On heating, it underwent isomeric change into benzoylphenyl-α-naphthylamine (m. p. 148—150°; identical with an authentic specimen).

N-*Methylbenziminophenyl ether* was prepared by Hantzsch's method (*Ber.*, 1893, **26**, 926) from benzmethylamideiminochloride and solid sodium phenoxide. It was obtained as colourless crystals, m. p. 30—31° (Found : N, 6·5. $C_{14}H_{13}ON$ requires N, 6·6%). On hydrolysis with 50% sulphuric acid, phenyl benzoate (m. p. 69—70°; not depressing the m. p. of an authentic specimen) was obtained. This imino-ether also decomposed without undergoing isomeric change.

N-*Phenyl*-o-*chlorobenziminophenyl ether*, prepared from o-*chlorobenzanilideiminochloride* (yellow prisms, m. p. 59°, b. p. 235°/60 mm.), formed colourless plates, m. p. 100° (Found : N, 4·8. $C_{19}H_{14}ONCl$ requires N, 4·55%).

N-*Phenyl*-p-*chlorobenziminophenyl ether*, from p-*chlorobenzanilide*

iminochloride (b. p. 219°/17 mm.), formed pale yellow crusts, m. p. 64—65° (Found : N, 4·3%).

N-*Phenyl*-2 : 4 : 6-*trichlorobenziminophenyl ether*, colourless prisms, m. p. 94—95° (Found : N, 3·5. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

N-*Phenyl*-p-*methoxybenziminophenyl ether*, m. p. 86—87° (Found : N, 4·4. $C_{20}H_{17}O_2N$ requires N, 4·6%). This compound appeared to be dimorphous. On crystallisation from alcohol, long needles first appeared. These gradually dissolved and were replaced by stout prisms. No difference in the m. p.'s of the two forms was observed.

N-*Phenyl*-o-*nitrobenziminophenyl ether*, thin leaves, m. p. 141—142° (Found : N, 9·0. $C_{19}H_{14}O_3N_2$ requires N, 8·8%). Heated for 2 hours at 230—240°, the material remained practically unchanged. Above this temperature it decomposed, yielding a coke-like residue.

N-*Phenyl*-p-*nitrobenziminophenyl ether*, long, yellow prisms, m. p. 102—102·5° (Found : N, 8·55%).

Benzoyl-2 : 4-*dichlorodiphenylamine*, obtained by heating either *N*-phenylbenzimino-2 : 4-dichlorophenyl ether or *N*-2 : 4-dichlorophenylbenziminophenyl ether, formed crusts, m. p. 109° (Found : N, 4·2. $C_{19}H_{13}ONCl_2$ requires N, 4·1%).

Benzoyl-2 : 4 : 6-*trichlorodiphenylamine* was prepared from *N*-phenylbenzimino-2 : 4 : 6-trichlorophenyl ether and *N*-2 : 4 : 6-trichlorophenylbenziminophenyl ether and obtained in long prisms, m. p. 149° (Found : N, 3·75. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

Benzoyl-o-*methoxydiphenylamine*, prepared from *N*-phenylbenzimino-*o*-anisyl ether, formed hard crusts, m. p. 117° (Found : N, 4·7. $C_{20}H_{17}O_2N$ requires N, 4·6%).

Benzoyl-p-*methoxydiphenylamine*, obtained from either *N*-phenylbenzimino-*p*-anisyl ether or *N*-*p*-anisylbenziminophenyl ether, formed slender prisms, m. p. 121° (Found : N, 4·8%).

Contrary to the statement of Mumm, Hesse, and Volquartz (*loc. cit.*), *N*-phenylbenzimino-*o*-nitrophenyl ether underwent isomeric change at 165°. The dark oil obtained by heating this imino-ether (10 g.) for 1 hour at 165° was covered with ether; *benzoyl*-o-*nitrodiphenylamine* (4 g.) slowly crystallised in yellowish leaves, m. p. 134° (unchanged by recrystallisation from alcohol) (Found : N, 8·8. $C_{19}H_{14}O_3N_2$ requires N, 8·8%).

Benzoyl-p-*acetyldiphenylamine*, prepared from *N*-phenylbenzimino-*p*-acetylphenyl ether, formed leaves, m. p. 136—137·5° (Found : N, 4·4. $C_{21}H_{17}O_2N$ requires N, 4·45%).

Each of the following five amides was prepared by heating the corresponding imino-ether, and also from diphenylamine and the appropriate acid chloride.

o-*Chlorobenzoyldiphenylamine*, large prisms, m. p. 142—143° (Found : N, 4·8. $C_{19}H_{14}ONCl$ requires N, 4·55%).

p-*Chlorobenzoyldiphenylamine*, fine leaves, m. p. 138—138·5° (Found : N, 4·3%).

2 : 4 : 6-*Trichlorobenzoyldiphenylamine*, flat prisms, m. p. 118—119° (Found : N, 3·6. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

p-*Methoxybenzoyldiphenylamine*, prisms, m. p. 139—140° (Found : N, 4·3. $C_{20}H_{17}O_2N$ requires N, 4·6%).

p-*Nitrobenzoyldiphenylamine*, yellow prisms, m. p. 156—157° (Found : N, 9·05. $C_{19}H_{14}O_3N_2$ requires N, 8·8%).

2 : 4 : 6-*Trichlorobenzanilide*, prepared from 2 : 4 : 6-trichlorobenzoyl chloride and aniline, formed long needles, m. p. 197° (Found : N, 4·4. $C_{13}H_8ONCl_3$ requires N, 4·7%).

Comparison of the Rates of Change of the Imino-ethers.—The comparison was made by measuring the amount of change which took place when each compound was heated for a given time at a definite temperature. Test-tubes, each containing 2 g. of an imino-ether, were immersed together for the standard time (90 minutes) in a thermostat, strictly comparable results thus being obtained even if slight fluctuations occurred in the temperature.

As many of the mixtures thus obtained exhibited great reluctance to crystallise from the fused material, analysis by melting- or freezing-point methods was excluded, and therefore the following chemical method was adopted.

About 0·5 g. of the mixture was weighed into a stoppered flask and dissolved in dry ether, 25 c.c. of an approximately *N*/5-solution of sulphuric acid in dry ether were added, and the mixture was kept for 3 hours to permit complete separation of the imino-ether sulphate as crystals or as an oil. The liquid was then filtered into a separating funnel containing water, the residue and the filter were washed with a little dry ether, and the contents of the funnel were shaken and titrated with *N*/5-sodium hydroxide and phenolphthalein. The difference between this titration and a blank, in which 25 c.c. of the standard acid were used, corresponded with the amount of imino-ether in the weighed material. The estimation was carried out in duplicate.

Control experiments showed that this process gave results agreeing to within a few units % with the calculated figure, the imino-ether sulphate being assumed to have the formula $RO{\cdot}CR{:}NR,H_2SO_4$. The error appeared to be constant for each imino-ether and the results in the tables below have been corrected accordingly—the corrections do not affect the arrangement of the imino-ethers in order of ease of isomeric change.

The imino-ethers containing the 2 : 4 : 6-trichlorophenyl group and *N*-phenylbenzimino-*o*-nitrophenyl ether did not give insoluble sulphates by this method, and the products obtained from them

were examined separately. In the case of *N*-phenylbenzimino-2 : 4 : 6-trichlorophenyl ether, the melting points of the heated samples were compared with those of known mixtures of the imino-ether and benzoyl-2 : 4 : 6-trichlorodiphenylamine. The products from the *N*- and *C*-trichlorophenyl compounds were crystallised from alcohol, and the unchanged compounds weighed. *N*-Phenylbenzimino-*o*-nitrophenyl ether underwent rearrangement at so low a temperature as to leave no doubt as to its position in the series.

The change of *N*-phenylbenziminomethyl ether was studied separately by Lander's method (J., 1903, **83**, 406) : 10 g., heated in a sealed tube at 300—330° for 2 hours, gave 2·5 g. of benzoylmethylaniline (m. p. after recrystallisation 57° ; did not depress the m. p. of an authentic specimen).

The results obtained were as follows :

O-*Substituted ethers*, RO·CPh:NPh.

	Percentage changed in 90 mins. at						
Group (R) on O atom.	162—163°.	200—201°.	219—220°.	242—243°.	255°.	266—267°.	300—330°.
o-Nitrophenyl	>40						
2 : 4 : 6-Trichlorophenyl	0	87	>91				
p-Acetylphenyl		39	76	92			
2 : 4-Dichlorophenyl		28	60	93			
o-Chlorophenyl		16	27	77	91		
m-Chlorophenyl				63	84		
p-Chlorophenyl				46	62		
α-Naphthyl					62	80	
β-Naphthyl					61	82	
Phenyl				25	45	71	
o-Anisyl					47	74	
m-Anisyl					43	55	
p-Anisyl					25	44	
Methyl							25

N-*Substituted ethers*, PhO·CPh:NR.

Group (R) on N atom.	% Change in 90 mins. at 267°.	270°.	Group (R) on N atom.	% Change in 90 mins. at 267°.	270°.
2 : 4 : 6-Trichlorophenyl	<17	—	*p*-Chlorophenyl	56	61
2 : 4-Dichlorophenyl	31	36	α-Naphthyl	61	63
o-Chlorophenyl	37	39	Phenyl	69	75
m-Chlorophenyl	47	49	*p*-Anisyl	80	85

C-*Substituted ethers*, PhO·CR:NPh.

Group (R) on C atom.	% Change in 90 mins. at 267°.	270°.	Group (R) on C atom.	% Change in 90 mins. at 267°.	270°.
p-Nitrophenyl	49	49	*p*-Chlorophenyl	61	62
2 : 4 : 6-Trichlorophenyl	<50	<55	Phenyl	69	75
o-Chlorophenyl	63	63	*p*-Anisyl	85	84

Benzoyl-2 : 4 : 6-trichlorodiphenylamine and benzoyl-*p*-methoxydiphenylamine were unchanged after heating for 1 hour at 240—250°

and 250—270°, respectively, showing that the isomeric changes into these compounds were not appreciably reversible.

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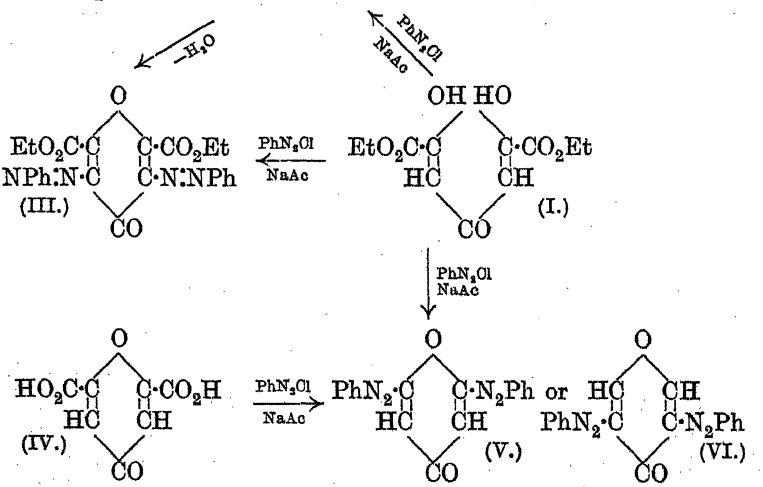
THE UNIVERSITY, SHEFFIELD. [*Received, May 3rd*, 1927.]

CCXXVIII.—*The Action of Diazonium Salts on Pyrones and their Parent Substances. Part I.*

By REGINALD THOMAS MULLEN and WILLIAM HAUGHTON CROWE.

IN connexion with the unsettled question of the constitution of mixed aliphatic aromatic azo-compounds, evidence in favour of the azo-structure has now been obtained, since ethyl acetonedioxalate (I), on treatment with benzenediazonium chloride in presence of sodium acetate, yields a mixture of *ethyl dibenzeneazoacetonedioxalate* (II) and *ethyl dibenzeneazochelidonate* (III). The former, on boiling with alcohol, loses water, ethyl dibenzeneazochelidonate being formed, with an ease that suggests the azo-structure.

$CO_2Et{\cdot}CO{\cdot}CH(N_2Ph){\cdot}CO{\cdot}CH(N_2Ph){\cdot}CO{\cdot}CO_2Et$ (II.)



Chelidonic acid (IV) reacts with benzenediazonium chloride to give an azopyrone (V or VI), formula (V) being the more probable because this substance could not be obtained by hydrolysis of the ester (III). The azopyrone was also formed to some extent during

the reaction between benzenediazonium chloride and ethyl acetonedioxalate. The replacement of carboxyl by azo-groups has been observed in other cases (compare Japp and Klingeman, J., 1888, **53**, 519; Bamberger, *Ber.*, 1892, **25**, 3547).

In the presence of sodium acetate, benzenediazonium chloride reacts with 2 : 6-dimethylpyrone and with diacetylacetone to give 3-*benzeneazo*-2 : 6-*dimethylpyrone* and 3 : 5-*dibenzeneazo*-2 : 6-*dimethylpyrone*, respectively.

Experimental.

Ethyl Dibenzeneazoacetonedioxalate (II).—Ethyl acetonedioxalate (prepared by Claisen's method, *Ber.*, 1891, **24**, 111, which gives a better yield than Willstätter's, *Ber.*, 1904, **37**, 3734) (7·8 g.) was added to an aqueous solution of benzenediazonium chloride (from aniline, 5 g., and hydrochloric acid, 13 c.c.). Addition of alcohol (59 c.c.) and much sodium acetate produced a heavy, red precipitate, which was filtered off and thoroughly washed by grinding with water; the aqueous-alcoholic filtrate slowly deposited a chocolate-coloured substance. The red product was crystallised from 80% alcohol and then from benzene–light petroleum (40% benzene), large, dark red prisms, m. p. 130°, soluble in organic solvents, being obtained (Found: C, 59·2; N, 12·0. $C_{23}H_{22}O_7N_2$ requires C, 59·2; N, 12·0%).

Ethyl Dibenzeneazochelidonate (III).—When the red precipitate formed by diluting the alcoholic filtrate from the crystallisation of the foregoing substance with water was crystallised from benzene–light petroleum, red needles were obtained, m. p. 117°, of a substance which was identical with that formed when ethyl dibenzeneazoacetonedioxalate was boiled with alcohol and the product crystallised (Found: C, 61·4; H, 4·5; N, 12·5. $C_{23}H_{20}O_6N_4$ requires C, 61·6; H, 4·5; N, 12·5%). It was readily soluble in organic solvents.

2 : 6-*Dibenzeneazopyrone*.—The chocolate-brown substance mentioned above crystallised from alcohol in chocolate-brown prisms, m. p. 131°, which were soluble in the common organic solvents (Found: N, 18·4. $C_{17}H_{12}O_2N_4$ requires N, 18·4%).

Action of Benzenediazonium Chloride on Chelidonic Acid.—Chelidonic acid (3 g.), obtained by repeatedly evaporating ethyl acetonedioxalate with concentrated hydrochloric acid (Claisen, *loc. cit.*), was added to a solution of benzenediazonium chloride (aniline, 5 g.; hydrochloric acid, 13 c.c.; water, 30 c.c.: sodium nitrite, 5 g.; water, 15 c.c.). The brown precipitate obtained on addition of an excess of sodium acetate crystallised from alcohol in chocolate-brown prisms, m. p. 131° (Found: C, 67·1; H, 3·6; N, 18·4%). A mixed-melting point proved this substance to be 2 : 6-dibenzeneazopyrone (above).

3-*Benzeneazo*-2 : 6-*dimethylpyrone*.—A solution of benzenediazonium chloride at 0° (aniline, 13 g.; hydrochloric acid, 26 c.c.; water, 60 c.c.: sodium nitrite, 13 g.; water, 30 c.c.) was treated with dimethyl pyrone (6 g.) and then with sodium acetate. After 2 days, the tarry product was filtered off and extracted several times with light petroleum–benzene (90% light petroleum); the *pyrone* obtained from the extract crystallised from light petroleum–benzene in yellow leaflets, m. p. 92° (Found : N, 12·5. $C_{13}H_{12}O_2N_2$ requires N, 12·3%).

3 : 5-*Dibenzeneazo*-2 : 6-*dimethylpyrone*.—To a solution of benzenediazonium chloride (aniline, 4·3 g.; hydrochloric acid, 9 c.c.; water, 20 c.c. : sodium nitrite, 4·3 g., in water, 10 c.c., was added until a blue colour was obtained on starch–iodide paper), diacetylacetone (2·5 g., prepared by boiling dimethylpyrone with baryta, acidifying the solution, and extracting it with ether; *Annalen*, 1890, **251**, 256) was added, followed by sodium acetate. The solution became yellow and then a light red substance was slowly precipitated. After 12 hours, this was filtered off, washed with cold water, and crystallised from benzene, from which it separated in light red needles, m. p. 150° (Found : N, 16·8. $C_{19}H_{16}O_2N_4$ requires N, 16·9%). It was soluble in organic solvents, but insoluble in water.

The authors wish to express their indebtedness to Professor J. N. Collie, F.R.S., and Professor A. W. Stewart for their interest in this research.

THE DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST.

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CCXXIX.—*Metallic Hydroxy-acid Complexes. Part IV. Complexes formed by Copper with the Monobasic Monohydroxy-acids.*

By IAN WILLIAM WARK.

THE author has suggested (J., 1923, **123**, 1816) that the stability of the metallic derivatives of a hydroxy-acid may be expected to increase with the acidity of the hydroxylic hydrogen. Thus, although the derivatives of lactic acid (*loc. cit.*) and of glycollic acid (Pickering, J., 1911, **99**, 1347) are easily hydrolysed, it was anticipated that the increased acidity of the hydroxyl group in mandelic and salicylic acids would lead to the formation of more stable complexes. These conclusions have now been verified experimentally.

It has previously been shown that the composition of sodium cuprilactate is most probably $Na_2[(\cdot O\cdot CHMe\cdot CO_2\cdot)_2Cu]$. In order to ascertain whether this compound is representative of a general series formed by the simpler hydroxy-acids, some work with the complexes formed by glycollic, mandelic, and salicylic * acids has been undertaken, and has established the fact that sodium cuprilactate is a definitely representative compound.

After a satisfactory general method of attack had been devised, it seemed desirable to ascertain whether the dihydroxy-phenols and the amino-acids would yield to a similar treatment. Accordingly, the copper derivatives of pyrocatechol and glycine were treated in alcoholic solution with sodium methoxide. Although blue complexes were formed in each case, no stable derivative could be isolated; and the complexes readily decomposed with the precipitation of cuprous or cupric oxide. Cupric phenylglycine is practically insoluble in a solution of sodium methoxide.

The constitution of the complexes will be discussed in a subsequent communication.

Experimental.

A. *Preparations in Aqueous Solution.*

Cuprimandelates.—Cupric *i*-mandelate (Winkler, *Annalen*, 1836, **18**, 320), which is anhydrous when dried at 100°, was obtained as a pale blue, sparingly soluble monohydrate by mixing solutions of sodium mandelate and cupric chloride [Found: Cu, 16·3; H_2O, 5·2. $Cu(C_8H_7O_3)_2,H_2O$ requires Cu, 16·6; H_2O, 4·7%].

Action of alkali on cupric mandelate. Since cupric mandelate is not wetted by water, it was necessary to wet it with alcohol in order to effect solution in alkali. Two equivs. of caustic soda ($N/2$) dissolve 1 mol. of the mandelate, presumably according to the equation $2NaOH + Cu(C_8H_7O_3)_2 = 2H_2O + Na_2[Cu(C_8H_6O_3)_2]$. This solution deposits cupric hydroxide on standing. It may be stabilised by the addition of excess of sodium mandelate [compare cupric lactate (*loc. cit.*, where the reasons for this stabilising effect have been discussed)].

After the addition of slightly less than two equivs. of caustic soda, the solution becomes alkaline to phenolphthalein, but provided that

* The aromatic β-hydroxy-acids of the salicylic acid type resemble the aliphatic α-hydroxy-acids with respect to complex formation (Weith, *Ber.*, 1876, **9**, 342; Pickering, J., 1912, **101**, 174; Beilstein, 3rd Edn., II, 1492; Piria, *Ann. Chem. Pharm.*, 1855, **17**, 262). Piria states that cupric salicylate readily gives moderately stable derivatives, $K_2[Cu(C_7H_4O_3)_2],4H_2O$ and $Ba[Cu(C_7H_4O_3)_2],4H_2O$, resembling the above cuprilactate, but he gives no experimental detail or analytical figures in support of this contention. Kahlenberg (*Z. physikal. Chem.*, 1895, **17**, 577) has found that, in the presence of sulphate ions, the concentration of the copper ions in a solution containing the complex cuprisalicylate is of a low order of magnitude.

a sufficient excess of the sodium mandelate is present, further addition of caustic soda does not precipitate cupric hydroxide, even in boiling solution. Such an alkaline solution, however, readily oxidises glucose.

Salts of Cuprimandelic Acid.—I. *Sodium cuprimandelate,* $Na_2[Cu(C_8H_6O_3)_2]$.

The chemistry of this compound is discussed in Section B.

II. *Sodium hydrogen cuprimandelate,* $NaH[Cu(C_8H_6O_3)_2]$. A concentrated solution of 1 mol. of cupric mandelate in 2 mols. of caustic soda, which has been stabilised by the addition of sodium mandelate, deposits slowly on standing a copious crop of fine, pale blue crystals. These are but slightly soluble in water. Analysis showed them to contain sodium and copper in the proportion 1 : 1, whereas the synthetic proportion was 2 : 1 {Found : Na, 5·2; Cu, 13·4; H_2O, 15·6. $NaH[Cu(C_8H_6O_3)_2],4H_2O$ requires Na, 5·0; Cu, 13·8; H_2O, 15·7%}. Evidently as the compound separates some alkali is liberated; if the solution is exposed to the air, carbon dioxide is absorbed and crystals of sodium carbonate begin to form. This compound is regarded as an acid salt, for 1 mol. of caustic soda dissolves it according to the equation $NaH[Cu(C_8H_6O_3)_2] + NaOH = Na_2[Cu(C_8H_6O_3)_2] + H_2O$, but again, on evaporation, the pale blue acid salt crystallises out. Cuprimandelic acid must be considered a fairly weak acid if carbonic acid is able to extract some of the alkali from its normal salt in this way, even when allowance is made for the fact that the acid salt is rather sparingly soluble.

III. *Silver cuprimandelate.* A neutral solution of sodium cuprimandelate, prepared by treating an excess of cupric mandelate * with caustic soda solution, is rapidly filtered into a solution of the calculated quantity of silver nitrate; a pale blue precipitate of *silver cuprimandelate* is formed immediately: $Na_2[Cu(C_8H_6O_3)_2] + 2AgNO_3 = 2NaNO_3 + Ag_2[Cu(C_8H_6O_3)_2]$. The salt is quite stable on boiling, but darkens after exposure to light for several months {Found : Ag, 36·8; Cu, 11·4. $Ag_2[Cu(C_8H_6O_3)_2]$ requires Ag, 37·3; Cu, 11·0%}. (The author is indebted to Mr. W. J. Lawrence for this analysis and that of the following mercurous salt.)

IV. *Mercurous cuprimandelate* may be prepared in a like manner to the silver salt, which it resembles in appearance {Found : Hg, 47·4; Cu, 7·2. $Hg_2[Cu(C_8H_6O_3)_2],5H_2O$ requires Hg, 46·9; Cu, 7·4%}. On prolonged heating, the mercury volatilises with the water of crystallisation, leaving pure cupric mandelate.

V. *Ferric cuprimandelate* also may be prepared by double decomposition. If excess of ferric chloride be present, a yellow or red solution is formed. With calculated quantities of the reagents, a

* It is advisable to use only small quantities of the cupric mandelate and to work rapidly, for the solution of sodium cuprimandelate is somewhat unstable

yellowish-brown, crystalline precipitate forms on boiling {Found : Fe, 7·5; Cu, 12·7; H_2O, 16·8. $Fe_2[Cu(C_8H_6O_3)_2]_3,14H_2O$ requires Fe, 7·7; Cu, 13·1; H_2O, 17·3%}.

VI. *Cupric cuprimandelate* was prepared as a pale blue, crystalline powder by double decomposition {Found : Cu, 29·3.

$$Cu[Cu(C_8H_6O_3)_2]$$

requires Cu, 29·6%}. There was no loss in weight on heating to 130°.

B. *Preparations in Non-aqueous Solvents.*

The main difficulties encountered in the present work arise from the ease with which the complexes are hydrolysed. Hence it was decided to use cupric salicylate, which is soluble in alcohol, acetone, and even chloroform, and exclude all traces of water. Later, it was found possible to deal in a similar manner with the mandelate, glycollate, and lactate, although they themselves are practically insoluble in these solvents.

I. *Sodium Cuprisalicylate.*—As a starting point, normal cupric salicylate is readily obtained by the method outlined by Pickering (*loc. cit.*). Piria (*loc. cit.*) has reported that this compound easily breaks down into free salicylic acid and the basic salicylate. Indeed, on prolonged heating at 110°, some of the acid volatilises, leaving dark brown patches of the basic salt, which should be regarded as the cupric salt of cuprisalicylic acid, $Cu[Cu(C_7H_4O_3)_2]$. Normal cupric salicylate crystallises both from alcohol and from acetone with solvent of crystallisation. Solutions in both solvents readily deposit dull green crystals of the basic salt. To a solution of cupric salicylate in ethyl alcohol was added an alcoholic solution of sodium ethoxide, such that the proportion was approximately 2Na : Cu. A pale green crystalline precipitate formed immediately and was collected, washed, and dried over concentrated sulphuric acid in a vacuum desiccator. It is soluble in water but rapidly undergoes hydrolysis to cupric hydroxide {Found : Cu, 16·3; Na, 12·3. $Na_2[Cu(C_7H_4O_3)_2]$ requires Cu, 16·6; Na, 12·1%}.

II. *Sodium Cuprimandelate.*—It was pointed out in Section A that disodium cuprimandelate cannot be isolated readily from its aqueous solution. It can, however, be obtained by dissolution of 1 mol. of anhydrous cupric mandelate in an alcoholic solution of 2 mols. of sodium ethoxide :

$$2NaOEt + Cu(C_8H_7O_3)_2 = Na_2[Cu(C_8H_6O_3)_2] + 2EtOH.$$

This solution was rapidly filtered while hot, and on standing overnight pale blue crystals separated {Found : Na, 9·2; Cu, 12·7. $Na_2[Cu(C_8H_6O_3)_2],2C_2H_5{\cdot}OH$ requires Na, 9·2; Cu, 12·7%}. The loss in weight on drying at 90° was 17·8% (Calc. for $2C_2H_5{\cdot}OH$, 18·3%); at 100° the compound gradually decomposed giving the odour of benzaldehyde.

III. *Sodium Cupriglycollate.*—Cupric glycollate, the starting point, has been described by Pickering (J., 1911, **99**, 1347), Fahlburg (*J. pr. Chem.*, 1873, **7**, 339), and Heintz (J., 1861, **14**, 439). Pickering and Kahlenberg (*loc. cit.*) have both investigated the action of aqueous alkalis upon this salt. Pickering came to the conclusion that for the formation of a neutral complex the ratio KOH : Cu was 1·64, and by the addition of alcohol he precipitated from the colloidal solution so formed an emulsion in which K : Cu = 1 : 1. These conclusions, if verified, would stamp the glycollate as being quite exceptional. Pickering also described a strongly alkaline compound in which the proportion was 2K : Cu.

Finely powdered, anhydrous cupric glycollate, although it dissolves in an alcoholic solution of sodium ethoxide, readily gives rise to an insoluble derivative. Consequently, sodium methoxide was substituted: $2NaOMe + Cu(C_2H_3O_3)_2 = Na_2[Cu(C_2H_2O_3)_2] + 2MeOH$. A fine crop of bright blue crystals formed over-night {Found: Na, 13·7; Cu, 19·0; loss at 110°, 23·2. $Na_2[Cu(C_2H_2O_3)_2],2\frac{1}{2}CH_3{\cdot}OH$ requires Na, 13·6; Cu, 18·8; $2\frac{1}{2}CH_4O$, 23·7%}. At temperatures higher than 110°, decomposition occurred. An aqueous solution deposited copper hydroxide in a few minutes.

IV. *Sodium Cuprilactate.*—The reactions of this compound in aqueous solution were discussed in an earlier paper (*loc. cit.*). Finely powdered, anhydrous cupric lactate, dissolved in the theoretical quantity of sodium ethoxide, deposits slowly on standing a pale violet, crystalline salt of low density {Found: Na, 12·8; Cu, 16·6; loss at 110°, 13·1. $Na_2[Cu(C_3H_4O_3)_2],2C_2H_6O$ requires Na, 12·2; Cu, 16·8; $2C_2H_6O$, 12·2%}. Heating to higher temperatures rapidly decomposed the compound.

C. *Measurements of Hydrogen-Ion Concentration.*

Darmois (*J. Phys. Radium*, 1924, [vi], **5**, 225), using the quinhydrone electrode, has investigated the action of caustic soda on cupric malate (compare J., 1923, **123**, 1831). He followed the effect produced by the gradual addition of alkali to a solution containing cupric malate, confirming the results of the work cited above. It seemed that this method, which owes its application to the fact that the electrode functions whilst there is still insufficient hydrogen present to allow the reaction $Cu^{\cdot\cdot} + H_2 = 2H^{\cdot} + Cu$ to proceed, would be useful in deciding quickly, without the necessity for laborious analyses such as have been outlined in the preceding sections, whether all these cupric salts behaved in a similar manner to the cupric mandelate, the derivatives of which were, at the time, the only series which had been investigated.

The method failed when any alkali metal was present, for the quinhydrone was oxidised and a deposit of cuprous oxide formed

However, some useful results were obtained before alkali had been added. According to the views advanced by the author, the cupric salts from which the complexes are derived are usually isomeric with the parent acids of the complexes themselves. Thus it was shown that cupric malate, $CuC_4H_4O_5$, is isomeric with cuprimalic acid, $H{\cdot}CuC_4H_3O_5$, and that in solution both compounds exist side by side. Likewise one might expect isomerism between cupric lactate and cuprilactic acid, cupric salicylate and cuprisalicylic acid, etc. Hence it seemed advisable to estimate roughly the hydrogen-ion concentrations in solutions of the various cupric salts under investigation. The quinhydrone electrode is useful for this purpose, and the results were checked by means of indicators, as shown in the following table.

	Cupric salt employed.	Salicylate.	Glycollate.	Lactate.
p_H	By indicators	4	5	5
	By quinhydrone–quinol electrode	3·5	4·7	4·7

Cupric salicylate is markedly acidic compared with the glycollate or lactate. One might expect, therefore, that cuprisalicylic acid would be a stronger acid than cuprilactic or cupriglycollic acid, and that its salts would be more stable—a prediction abundantly verified by experiment. It is unfortunate that cupric mandelate is not sufficiently soluble to enable a comparison with the other salts to be made.

Summary.

1. It has been shown that several monobasic monohydroxy-acids, *viz.*, lactic, mandelic, glycollic, and salicylic acids, all give rise to similar copper-containing complex acids.

2. The sodium salts of these complex acids have been isolated from alcoholic solutions. Their formulæ are of the type

$$Na_2[(\cdot O\cdot CHR\cdot CO_2\cdot)_2Cu]$$

and they all hydrolyse readily in aqueous solution.

3. The derivatives of cuprimandelic acid, which are more stable in aqueous solutions than most of the other complexes, have been investigated more fully.

4. The hydrogen-ion concentrations in solutions of the cupric salts of lactic, glycollic, and salicylic acids have been estimated.

The author wishes to express his thanks to the Commissioners for the Exhibition of 1851 for a Scholarship which enabled him to carry out that portion of the work which was performed in California.

THE UNIVERSITIES OF CALIFORNIA AND SYDNEY.

[*Received, March 21st*, 1927.]

CCXXX.—*The System Ferric Oxide–Arsenic Acid–Water at Low Concentrations of Arsenic Acid.*

By NORMAN HOLT HARTSHORNE.

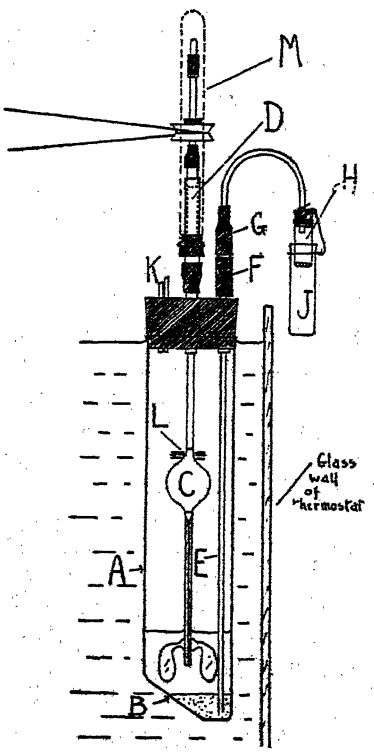
THIS work was undertaken (*a*) to discover whether any of the numerous ferric arsenates described in the literature were merely stages in a series of adsorption compounds, as in the case of the ferric phosphates (Carter and Hartshorne, J., 1923, **123**, 2223); and (*b*) to test the usefulness of the viscometer-stirrer employed by the author to determine the transition points of salt hydrates (J., 1924, **125**, 2097) in the investigation of ternary systems. It was thought that this apparatus would afford a rapid means of determining the attainment of equilibrium, thus avoiding the wastage involved in test analyses, and that the curves obtained by plotting the time of flow of the saturated solutions against the concentration of one of the components would show breaks indicating the limits of stability of the various solid phases, thus saving some of the laborious analyses inherent in heterogeneous equilibrium work.

Metzke (*Z. anorg. Chem.*, 1899, **19**, 457) describes the following ferric arsenates: The basic salts, $3Fe_2O_3,2As_2O_5,17$ and $16{\cdot}5H_2O$; $4Fe_2O_3,3As_2O_5$, 33·5, 20·5, and $15{\cdot}4H_2O$, the last approximating to the naturally occurring pharmacosiderite; the neutral salts $Fe_2O_3,As_2O_5,10,9,4$ (artificial scorodite), and $1H_2O$; the acid salts $2Fe_2O_3,3As_2O_5,22{\cdot}5H_2O$ and $Fe_2O_3,3As_2O_5,16{\cdot}7H_2O$. He accepts the view that the acids corresponding to these salts are formed from As_2O_5 by the replacement of the oxygen atoms by hydroxyl groups. On this basis, a compound of the type $5Fe_2O_3,3As_2O_5$ is missing, but Metzke thinks it possible that the compounds $3Fe_2O_3,2As_2O_5,17$ and $16{\cdot}5H_2O$ are mixtures of this pentabasic salt with one less basic. Verneuil and Bourgeois (*Compt. rend.*, 1880, **90**, 223) also prepared artificial scorodite, whilst Duncan (*Pharm. J.*, 1905, **20**, 223) describes the neutral salt $Fe_2O_3,As_2O_5,2H_2O$, which is dehydrated at 100°. Ježek and Siňek (*Z. Kryst. Min.*, 1914, **54**, 88) state that an anhydrous neutral salt is formed as a deposit of black prismatic crystals in the Deacon chlorine process. Other ferric arsenates, most of which approximate to those given above, are described by workers in the early part of the last century, notably Berzelius, but the inaccurate analytical methods available at that time and the exhaustive nature of Metzke's researches make it unnecessary to specify them. The following ferric arsenates occur in nature: pharmacosiderite, $4Fe_2O_3,3As_2O_5,15H_2O$; white iron-sinter, $2Fe_2O_3,As_2O_5,12H_2O$; and scorodite, $Fe_2O_3,As_2O_5,4H_2O$.

EXPERIMENTAL.

The system was studied at 25°. The apparatus used for preparing the equilibrium mixtures and collecting the phase samples is shown in Fig. 1. The solubility tube, A, was about 6 cm. wide and 26 cm. long, having a bottom so shaped as to collect the solid at the foot of the tube, E. This shape is very useful when (as was often the case in the present investigation) the amount of solid is small. It is important that the sloping portion, B, should be sufficiently steep. The viscometer-stirrer, C, was the same as that used in the previous work (*loc. cit.*), *i.e.*, with a capillary diameter of about 0·75 mm. It was supported by a glass bearing with thrust surfaces ground to a good fit and packed with vaseline contained in the tube, D. This type of bearing is simple to make, trustworthy, and sufficiently air-tight in cases where rigorous sealing of the solubility tube is unnecessary. Any vaseline which ran down the stem of the viscometer was caught by the rings of filter paper at L. These were changed occasionally and were quite effective in preventing contamination of the mixtures. The apparatus for collecting the phase samples is shown connected to the solubility tube by means of the rubber tube, F (which normally was closed by a piece of glass rod), and the sliding connexion, G. It consisted of the collecting tube, E, the weighed filter, H, and the weighing bottle, J, being thus merely a modification of the apparatus used previously for ferric and ferrous phosphates (*loc. cit.*; Carter and Hartshorne, J., 1926, 363), the most important difference being that it was not now necessary to filter the samples at thermostat temperature, since this was not far removed from that of the room. Dry air for forcing the samples through the filter was admitted through the tube, K. During this operation,

FIG. 1.



the stirrer bearing was sealed by the tube, M, after removal of the pulley. The samples were subsequently dissolved in hydrochloric acid and diluted to a standard volume. The solubility tube was supported in a glass-sided thermostat maintained at 25° ± 0·02° by means of an ordinary gas regulator.

Some difficulty was experienced in finding a suitable starting point for the preparation of the equilibrium mixtures. Arsenic acid ($H_3AsO_4,\frac{1}{2}H_2O$) was prepared by the oxidation of A.R. arsenious oxide (B.D.H.) according to the method described in Vanino's "Präparative Chemie," 1921, Vol. I, p. 215. Ferric hydroxide, prepared by the method used in the ferric phosphate work, could not, however, be dissolved in a solution of the arsenic acid; in spite of many variations in the conditions, only very small proportions were attacked. This is no doubt to be attributed to the small solubility of the ferric arsenates in arsenic acid, for in some cases microscopic examination showed that the ferric hydroxide particles were coated with arsenate, which prevented further action. It has been found that in solutions containing up to 22% of As_2O_5 the solubility at 25° never exceeds 0·1% of Fe_2O_3. The difficulty was eventually overcome by adding hydrochloric acid to the mixture. The ferric chloride thus formed reacted with the arsenic acid, and on repeated evaporation to dryness the ferric arsenate was freed from all but a trace of hydrochloric acid. The mixture, especially when concentrated, had a greenish-blue tint. On one occasion after an evaporation disc-shaped particles separated similar to those observed by Metzke (*loc. cit.*) when attempting to prepare artificial scorodite. The greenish-blue colour of these and other preparations is also mentioned by Metzke and is evidently due to a complex ferriarsenic acid or acids, analogous to the pink ferriphosphoric acids. This view is supported by the observations of Metzke and earlier workers, that the neutral and acid arsenates dissolve in concentrated ammonia, and by that of Duncan (*loc. cit.*), that oxidised solutions of ferrous arsenates respond very faintly to the thiocyanate test for ferric iron.

The mixture thus prepared was the basis of all the equilibrium mixtures studied. A portion, suitably diluted with water and freed from large lumps of solid, was transferred to the solubility tube, and after equilibrium had been reached and the necessary phase samples collected, water or syrupy acid was added and a new equilibrium reached, and so on.

Some difficulty had been anticipated in keeping the capillary of the viscometer clean. The method of washing with a few drops of water cannot be used in ternary systems of the present type, since the addition of water in large excess to most of the saturated

solutions results in the precipitation of neutral or basic salts. In the present work, a dilute solution of arsenic acid was found quite satisfactory as a wash liquid, and a few drops of this were blown down the viscometer from a wash-bottle every time the composition of the mixture was changed. Such a procedure was neither permissible nor necessary in order to obtain concordant results for successive readings of the same equilibrium. In order to provide for cases in which suitable wash liquids cannot be found for a ternary system, the author has devised an apparatus in which the stirrer and viscometer are separate, the latter being instantly removable for cleaning without disturbing the rest of the apparatus. So far, however, it has been found quite unnecessary to use it. Moreover, in ternary systems the temperature is kept constant, and consequently crystallisation in the capillary through temperature changes cannot occur. When readings are being taken with the viscometer, it is essential that the air expelled from the solubility tube by the falling liquid should be able to escape easily. In the previous work, the stirrer bearing provided an adequate leak, but in the present case it was found necessary to remove the glass plug from the tube, F (Fig. 1). When equilibrium was established the readings agreed to within 0·4 sec., and frequently to within 0·2 sec. The agreement is closer than in the previous work, but the percentage error remains about the same.

The analysis of the phase samples was effected as follows. The arsenic was separated by reduction with hydrazine and subsequent distillation as arsenious chloride. The apparatus used was that described by Jannasch and Seidel (*Ber.*, 1910, **43**, 1218), with the addition that the receiver was cooled in a large beaker of water and was furnished with a water trap to prevent any escape of arsenic. (These precautions are, however, probably unnecessary.) An aliquot part of the phase sample solution was measured into the distillation flask, concentrated hydrochloric acid was added until the volume was about 110 c.c., and the solution was saturated with hydrogen chloride; 3 g. of hydrazine sulphate and 1 g. of potassium bromide were then added, and the liquid was distilled until only 30—40 c.c. remained. The distillate was titrated as described below. High results are obtained unless the flame is screened from all but the bottom of the flask by an asbestos ring with a wire gauze centre: without this precaution, the flask becomes heated above the liquid and hydrazine distils over. The amount of arsenic in the reagents was found to be negligible. The use of a continuous stream of hydrogen chloride during the distillation was found, in agreement with Jannasch and Seidel, to be quite unnecessary for the complete volatilisation of the arsenic.

The distillate was titrated with potassium iodate solution, according to the method described in Scott's "Standard Methods of Chemical Analysis," 1922, Vol. I, p. 44. The iodate solution was standardised against resublimed A.R. arsenious oxide (B.D.H.). Owing to the distillation, the arsenious chloride solution was more dilute than is usual in this titration, and the reaction was consequently slower; it was therefore necessary to add the last few c.c. of the iodate very cautiously, waiting 5 minutes between each addition. As a check, the solution was titrated back with a standard arsenite solution, but the first drop almost invariably restored the colour to the chloroform.

The iron in the liquid phase was determined colorimetrically with ammonium thiocyanate—it never exceeded 0·1% as Fe_2O_3. In the solid phases, it was determined either (1) gravimetrically as oxide in the residue from the arsenic distillation, after decomposing the excess of hydrazine with nitric acid; (2) by titration of the residue with potassium dichromate, after removing the hydrazine with nitric acid and expelling the latter by evaporation; or (3) by direct titration of the phase sample solution with potassium dichromate. Stannous chloride was used as a reducing agent in the dichromate titrations. Methods (1) and (2) were both unsatisfactory because the weights of iron in the quantities of solution necessary to obtain a convenient amount of arsenious chloride were small. By using method (3) more solution could be titrated, and it was found by experiment that, provided the concentration of hydrochloric acid was not too high, the presence of the small amounts of arsenate involved did not appreciably affect the results. To ensure that the hydrochloric acid concentration was sufficiently low, the phase sample solutions were diluted with water before reduction by the stannous chloride, until in the cold the colour due to the ferric chloride was a pale yellow.

Results.

The results are in Table I. The composition of the phases is expressed in terms of Fe_2O_3 and As_2O_5, and, in the case of mixtures 1—13, as $FeAsO_4$ and H_3AsO_4 also. This second mode of expression is made possible by the absence of basic solid phases, and its object is to bring out more clearly the orientation of the conjugation lines when the results are plotted. If Fe_2O_3 and As_2O_5 are used as plotting components, the diagram is confined within an area which is very narrow in the direction $Fe_2O_3 \longleftrightarrow As_2O_5$, and its significance is difficult to appreciate. Mixtures 14—20 are not so treated because their percentages of Fe_2O_3 in the liquid phase were only determined approximately. Graphic expression is, however, not

TABLE I.

(Solid phase analyses marked with an asterisk refer to the *dried* solid, the remainder to the moist solid.)

		Liquid phase.				Solid phase.			
Mixture.	Time of flow (secs.).	% Fe_2O_3.	% As_2O_5.	% $FeAsO_4$.	% H_3AsO_4.	% Fe_2O_3.	% As_2O_5.	% $FeAsO_4$.	% H_3AsO_4.
1	81·7	Trace.	2·6	Trace.	3·2	10·3	17·0	25·1	2·7
2	82·6	„	3·5	„	4·3	10·8	18·2	26·3	3·3
3	83·4	„	4·4	„	5·4	9·6	17·1	23·4	4·1
4	84·5	„	5·4	„	6·7	13·7	23·3	33·4	4·45
5	85·0	„	5·8	„	7·2	10·9	20·9	26·6	6·4
6	85·7	„	6·4	„	7·9	15·8	27·9	38·5	6·4
7	86·6	0·001	7·96	0·001	9·83	—	—	—	—
8	89·0	0·004	10·11	0·01	12·47	4·1	15·2	10·0	11·5
9	92·1	0·01	12·49	0·02	15·40	5·5	18·74	13·4	13·4
10	97·4	0·036	16·19	0·088	19·93	—	—	—	—
11	102·0	0·037	18·82	0·090	23·17	2·7	21·22	6·6	21·41
12	108·0	0·059	21·77	0·14	26·78	3·4	24·94	8·3	24·75
13	110·6	0·076	23·13	0·185	28·42	26·8*	52·8*	65·4*	17·5*
14	87·4	Approximately 0·1	8·0			—	—		
15	87·4		8·4			—	—		
16	92·6		12·3			21·8*	58·6*		
17	94·1		13·2			—	—		
18	95·5		14·3			—	—		
19	96·7		14·9			—	—		
20	97·7		15·5			22·5*	57·9*		

Composition and Appearance of Solid Phases.—*Mixtures* 1—10: Fe_2O_3,As_2O_5,xH_2O, with adsorbed acid. Amorphous.

Mixtures 11—13: Fe_2O_3,As_2O_5,xH_2O (with adsorbed acid) + $Fe_2O_3,2As_2O_5,8H_2O$. Amorphous and needles.

Mixtures 14—20: $Fe_2O_3,2As_2O_5,8H_2O$ (Calc.: Fe_2O_3, 20·94; As_2O_5, 60·21%). Needles.

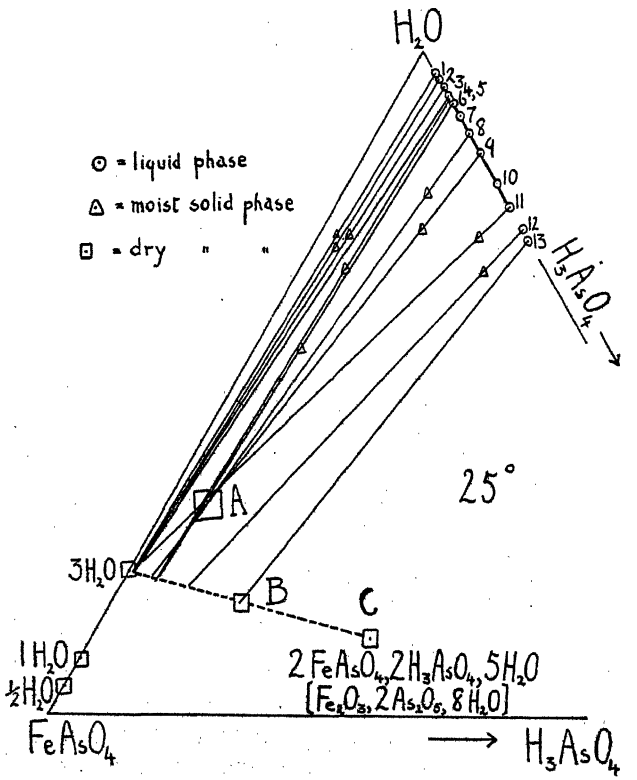
so necessary for those mixtures, for the compositions of their solid phases were found by analysis of the dried solid. Fig. 2 shows mixtures 1—13 plotted on a triangular diagram, and Fig. 3 shows the times of flow of the liquid phases (excluding mixture 13) plotted against their content of As_2O_5.

From Table I, it is seen that the percentage of ferric oxide in all the liquid phases is extremely small: even mixtures 14—20 which are metastable show only about 0·1%. It was feared at first that this small solubility would render the viscosity measurements useless through their not differing appreciably from those of aqueous arsenic acid solutions. The curves in Fig. 3 show, however, that mixtures 14—20 have a distinctly higher viscosity than the others at the same acid concentrations; on the assumption that the viscosity increases with solubility, this confirms the metastability of these

mixtures. Further, a distinct break occurs between mixtures 6 and 7, the significance of which is discussed later.

From Table I it will be seen that the mixtures 11—13 possessed the same two solid phases. It is evident that in these cases equilibrium was not attained, since theory demands that there shall be only one composition for a solution in equilibrium with any two

FIG. 2.

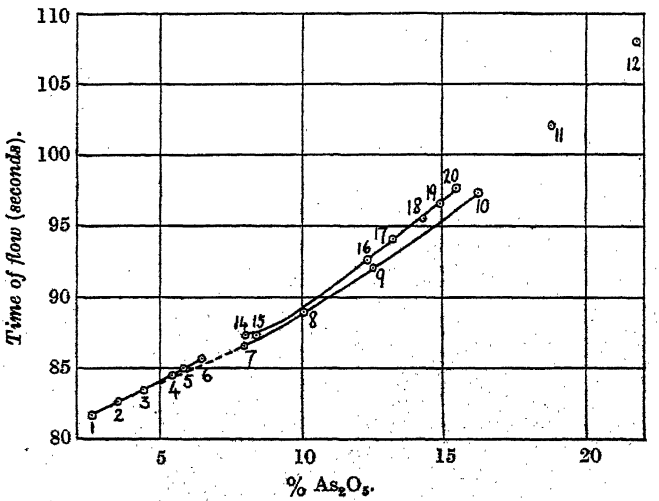


solid phases at constant temperature. This is not to be attributed to any failure to take the usual precautions to ensure the attainment of equilibrium, for the stable solid phase was presumably present in each case, and stirring was continued long after any change in the viscosity of the solution and in the appearance of the solid under the microscope had ceased (the mixtures were stirred for 35, 6, and 26 days, respectively). Rather must it be ascribed to an extreme sluggishness in approaching equilibrium. This was also experienced in the ferric phosphate work in this region, and is no doubt due to

the low solubility of the solid phases. In view of this, it is impossible to be certain to what extent equilibrium was reached in the other mixtures. The least doubt would appear to attach to mixtures 14—20 which possessed a single well-defined crystalline solid phase. These, however, were metastable.

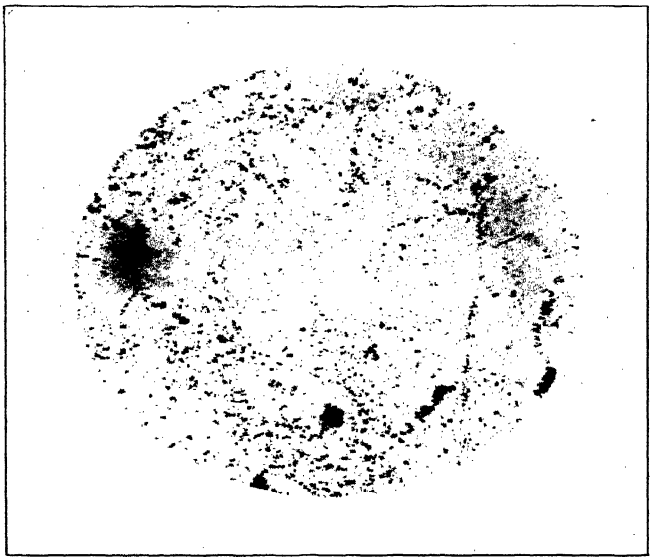
The solid phase of mixtures 1—10 was seen under the microscope to be very finely divided, the average diameter of the particles being 1·0—1·5 μ. Under crossed Nicols and an oil-immersion objective they showed no trace of colour and may therefore be described as amorphous. Fig. 4 is a photomicrograph of the solid phase of mixture 1 which is typical of the whole series. The conjugation lines

FIG. 3.



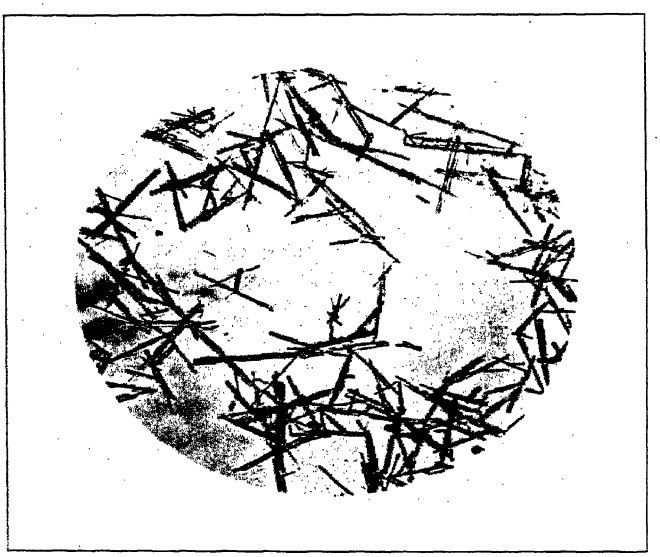
of these mixtures together with that of mixture 11, which for all practical purposes may be included with them since the proportion of acid salt which it contained was exceedingly small, suggest (see Fig. 2) that the solid is a neutral ferric arsenate containing varying amounts of adsorbed arsenic acid. In this respect the system is similar to the ferric phosphate system (*loc. cit.*). Marked adsorption is indeed to be expected in these cases, for the solid is finely divided and amorphous. This factor limits the value of any conclusions drawn from the conjugation lines, and further evidence is necessary to show where they end. In the present case an attempt to provide this was made by analysing the dried solid phase of mixture 13 (point B). This contained both the neutral arsenate and the acid salt $Fe_2O_3,2As_2O_5,8H_2O$ (point C), so that extrapolation of the line

FIG. 4.



Fe_2O_3,As_2O_5,xH_2O *and adsorbed acid.*
Average diameter of particles : 1·0—1·5 μ.

FIG. 5.



$Fe_2O_3,2As_2O_5,8H_2O$.
(× 260).

[*To face p.* 1767.]

CB gives information as to the water content of the former. As will be seen from the figure, this leads to the composition

$$FeAsO_4,3H_2O \text{ (or } Fe_2O_3,As_2O_5,6H_2O).$$

No great reliance can, however, be placed on the accuracy of the determination of the point B, since it is probable that the solid suffered some change in composition during the drying process on account of its fine state of division and the presence of adsorbed acid. (The solid was washed with anhydrous ether which was then removed in a current of dry air.)

It will be noticed that the lines fall into two groups, *viz.*, 1—4 and 5—11, the latter converging approximately on the point A. It does not appear, however, that this has any significance, for the point A is far removed from the line CB, and, moreover, no simple formula can be assigned to it. The break in the viscosity curve between mixtures 6 and 7 (see Fig. 3) may be due to a small change in the solid phase, but it is more probably due to incomplete attainment of equilibrium, especially as the order in which the mixtures were prepared was from Nos. 6 to 1 followed by a reversion to No. 7, *i.e.*, to the mixture on the other side of the break. Possibly the true course of the curve is as represented by the broken line drawn from 3 to 7.

If the conjugation lines reach as far as the line CB produced, the diagram shows that certain of them cross over the others. This, too, indicates that equilibrium was not attained, for it implies that a mixture of the three components lying within the crossing region has a choice of equilibrium states. A similar arrangement of lines was observed in the ferric phosphate work at 25° (*loc. cit.*, p. 2226), but its significance was not then appreciated. For the present, the solid phase in equilibrium with mixtures 1—10 is described as Fe_2O_3,As_2O_5,xH_2O (where x is probably not far removed from 6), containing adsorbed acid.

Mixtures 14—20 were made by stirring another portion of the starting material with arsenic acid solutions of progressively decreasing strengths. They were all metastable, as both the analyses and the viscosity curves show. The solid consisted of small needle-shaped crystals (see photomicrograph, Fig. 5) which could be easily filtered; they were dried by washing with ether and underwent no visible change. They were therefore analysed dry in two cases and the results are given in Table I. From these figures and from the crystalline form, it was concluded that they were $Fe_2O_3,2As_2O_5,8H_2O$, isomorphous with $Fe_2O_3,2P_2O_5,8H_2O$ (*loc. cit.*, p. 2230). The analytical figures are not as close to this composition as is desirable, but they do not agree with any other known or anticipated compound. The inaccuracy is probably due to the smallness

of the crystals, the relatively large surface magnifying the effect of incipient decomposition. The error is in the basic direction, which is in agreement with this explanation. This compound does not appear to have been described before. Its constitution and that of its phosphate analogue cannot be explained in any simple manner on the assumption that the salts are formed simply by the replacement of acid hydrogen by ferric iron. This is further evidence that the salts are complex. A formula analogous to that given by Weinland and Ensgraber to the phosphate would serve also for the arsenate, *viz.*, $[Fe(AsO_4)_2]H_3,2{\cdot}5H_2O$. No sign of Metzke's compound, $2Fe_2O_3,3As_2O_5,22{\cdot}5H_2O$, has been found.

Summary.

The system ferric oxide–arsenic acid–water has been studied between the concentrations 2·6 to 23·13% of As_2O_5 at 25°. Within this range the following solid phases have been found: The neutral salt, Fe_2O_3,As_2O_5,xH_2O (where x is probably not far removed from 6), carrying varying amounts of adsorbed arsenic acid; and the acid salt, $Fe_2O_3,2As_2O_5,8H_2O$, which has apparently not been described before. No basic salts were obtained. A feature of the system was the sluggishness with which equilibrium was approached even in the presence of the stable phase, and it is evident that in some cases it was not attained.

The author's stirrer-viscometer was used in this work in order to test its usefulness in the investigation of ternary systems. No difficulty was experienced in obtaining readings concordant to within 0·5% and frequently less. The system did not, however, afford much opportunity for making use of viscosity measurements.

In conclusion, the author wishes to express his thanks to Dr. J. F. Spencer for his helpful interest in this work.

BEDFORD COLLEGE,
UNIVERSITY OF LONDON. [*Received, April 2nd*, 1927.]

CCXXXI.—*The Preparation and Hydrolysis of the Isomeric β-Tolylethyl Bromides.*

By JOHN BALDWIN SHOESMITH and ROBERT JORDAN CONNOR.

IN a recent paper (Shoesmith and Slater, J., 1924, **125**, 2278), comprising one of a series of investigations on the polar and other factors which govern the reactivity of halogens in substituted halogenated benzenoid derivatives, the transmission of a powerful alternating influence from the methyl group of the tolyl radical

to halogen (*a*) directly attached to the same benzene nucleus and (*b*) removed by one carbon atom from the nucleus was demonstrated by the great difference in reactivity of the halogens in the isomeric iodotoluenes, $CH_3 \cdot C_6H_4I$, and ω-bromoxylenes, $CH_3 \cdot C_6H_4 \cdot CH_2Br$, and by the manner in which the order of ease of replacement of the bromine atoms in the latter case is dependent on the reagent used.

The interesting problem as to how far the influence of the methyl group extends beyond the benzene ring has now been investigated, the isomeric β-tolylethyl bromides having been prepared and submitted to the action of hydrolysing and reducing agents. The compounds are very different from the ω-bromoxylenes and very similar to one another in chemical and physical properties. They are quite stable towards aqueous alcohol at 76° and towards an aqueous acetic acid solution of hydrogen iodide. Differences in the rate of hydrolysis by aqueous-alcoholic sodium hydroxide have been observed and the order is : unsubs. (1·25) > *m*(0·83) > *p*(0·7) > *o*(0·6), but the differences are exceedingly small. (The figures in brackets denote the reciprocal of the time taken for half hydrolysis of the bromide at 76°, *i.e.*, an approximate rate of hydrolysis; compare Shoesmith and Slater, J., 1926, 214.) There appears to be a very slight residuum of alternating effect, and all the substituted compounds are slightly more difficult to hydrolyse than β-phenylethyl bromide—the reverse of the case in the corresponding benzyl bromides.

The *o*-isomeride is the most difficultly hydrolysable. The anomalous position of *o*-isomerides has been repeatedly stressed (as has also the fact that this is not due to steric influences; Shoesmith and Slater, J., 1926, 215). Olivier has arrived independently at the same conclusion (*Rec. trav. chim.*, 1926, **45**, 452, 710). As yet no satisfactory explanation has been given of the factors governing the reactivity of ortho-substituted benzyl bromides, save that there is here present an influence which renders them less reactive to hydrolysing and more reactive to reducing agents (*e.g.*, hydrogen iodide) than would be expected from any of the various theories put forward to explain enhanced and subdued reactivity.

It may now with certainty be concluded that those influences the effect of which was demonstrated so clearly in the isomeric ω-bromoxylenes are only feebly transmitted through the α-carbon atom of the side chain in the β-tolylethyl bromides, a conclusion of special interest in view of recent observations (Ing and Robinson, J., 1926, 1656; Goss, Hanhart, and Ingold, this vol., p. 250) that a very appreciable general effect due to positively charged nitrogen

is transmitted through two singly bound carbon atoms directly attached to the benzene nucleus.

EXPERIMENTAL.

The isomeric β-tolylethyl bromides were prepared according to the general scheme:

$$CH_3\cdot C_6H_4Br \xrightarrow{Mg} CH_3\cdot C_6H_4\cdot MgBr \xrightarrow{CH_2Cl\cdot CH_2\cdot OH} CH_3\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH \xrightarrow{PBr_5} CH_3\cdot C_6H_4\cdot CH_2\cdot CH_2Br.$$

The Isomeric β-Tolylethyl Alcohols.—Grignard's method (*Compt. rend.*, 1905, **141**, 44) was modified in several important particulars. To the bromotoluene (64 g., carefully freed from traces of possible phenolic impurities) in 250 c.c. of dry ether, 9 g. of magnesium were added and, when the vigorous reaction ended, dry, freshly distilled ethylene chlorohydrin (10 g.), dissolved in an equal volume of dry ether, was slowly dropped in. After the vigorous reaction had abated, the ether was distilled away and the residue was heated under 14 mm. pressure at a temperature not exceeding 180—200° for 2 hours to remove toluene, ditolyl, etc.; it was then mixed with ice and after 30 minutes the decomposition was completed by the addition of the calculated quantity of sulphuric acid in ice-water. The ethereal extract of this solution was dried, the ether distilled away, and the residue heated for about 10 minutes with aqueous-alcoholic potash. Extraction with ether, drying, and distillation, finally in a vacuum, then gave the β-tolylethyl alcohol in 20—24% yield, and no improvement could be effected. The alcohols had b. p.'s: *o*-isomeride, 115—116°/13 mm. (compare Grignard, *loc. cit.*); *m*-isomeride, 115—117°/13 mm. (Braun, Grabowski, and Kirschbaum, *Ber.*, 1913, **46**, 1266); and *p*-isomeride, 116·5—118°/14 mm. (Grignard).

The Isomeric β-Tolylethyl Bromides.—As hydrogen bromide has no effect on these alcohols, the bromides were prepared by adding phosphorus pentabromide (60 g.) to 15 g. of the respective β-tolylethyl alcohols, dissolved in 50 c.c. of dry benzene, the reaction being controlled by shaking in ice-water and completed by heating for 1 hour at a temperature not exceeding 50°. The mixture was then poured on excess of ice, and the bromide was extracted with ether, dried over sodium sulphate, and distilled in a vacuum. The distillate was washed with water to remove final traces of phosphoryl bromide, dried, and redistilled. The bromides all boiled, as expected, at a lower temperature than the corresponding alcohols. They had b. p.'s: *o*-compound, 99—100°/10 mm.; *m*-compound, 101—103°/11 mm.; and *p*-compound, 103·5—105°/11 mm. They con-

tained hydrolysable bromine: *o*-isomeride, 39·4; *m*-isomeride, 39·8; and *p*-isomeride, 40·3% ($C_9H_{11}Br$ requires hydrolysable Br, 40·2%). They are stable, sweet-smelling, non-pungent, non-lachrymatory oils, thus differing sharply from the corresponding ω-bromoxylenes.

β-Phenylethyl bromide was prepared from freshly distilled, commercial β-phenylethyl alcohol in a similar manner and, for comparative purposes, to make quite sure that only the *ethyl* bromides are formed by the action of phosphorus pentabromide on the alcohols, a sample was prepared by a method suggested to us by Professor Lapworth. A mixture of β-phenylethyl alcohol (20 g.) and constant-boiling hydrobromic acid (50 c.c.) was boiled under reflux for 4 hours. The bromide so formed was washed with water until free from halogen acid, dried, and distilled. The samples obtained by the two methods had identical boiling points, 89—89·5°/12 mm., estimations of hydrolysable bromine showed they were pure, and later the rate of hydrolysis showed they were identical.

Behaviour towards Hydrogen Iodide.—All the bromides were stable to hydrogen iodide in aqueous acetic acid at 100° for 4 hours. For comparative purposes, some unpublished observations, made in collaboration with Dr. R. H. Slater, on ω-bromo-*m*- and -*p*-xylenes are given in order to stress the differences observed in the two cases. These figures were obtained in a similar manner, but at 110° (experience has shown that slightly different results are obtained at the two temperatures); t, w, and x have the usual significance.

TABLE I.

	ω-Bromo-*m*-xylene.		ω-Bromo-*p*-xylene.*	
t (hrs.).	w.	x.	w.	x.
1	0·1239	69	0·1208	44
2	0·1245	87	0·1217	66
3	0·1225	100	0·1286	75

* The *p*-isomeride is not reduced by hydrogen iodide in glacial acetic acid at 25°. Its reduction at 110° shows the powerful reducing action of the aqueous acetic acid reagent at this temperature.

Hydrolysis of the Isomeric β-Tolylethyl Bromides.—The bromides were stable to aqueous alcohol at 76° for 4 hours. Comparative hydrolysis figures were obtained as follows: The bromide (approx. 0·50 g.) was dissolved in 75 c.c. of absolute alcohol, 25 c.c. of *N*/10-sodium hydroxide were added, and the volume was made up to 103 c.c. Aliquot portions (20 c.c.) were heated in a thermostat at 76° (b. p. of carbon tetrachloride) for definite times, and the amount

of hydrolysis which had taken place was estimated by titrating the unused alkali with standard hydrochloric acid. The results are in Table II.

TABLE II.

	o-Isomeride. $w = 0{\cdot}501$.	*m*-Isomeride. 0·506.	*p*-Isomeride. 0·500.	β-Phenylethyl bromide. 0·453.
t (hrs.).	*x*.	*x*.	*x*.	*x*.
½	38	45	46	56
1	54	63	56	68
2	69	75	71	81
4	82	86	83	89
6	85	90	87	93

The order of reactivity with *N*/30-alcoholic potassium hydroxide at 25° was exactly the same.

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EDINBURGH UNIVERSITY. [*Received, May 4th*, 1927.]

CCXXXII.—*Reduction of Silver Compounds in Alkaline Solution.*

By WALTER FARMER and JAMES BRIERLEY FIRTH.

THE object of the present investigation was to ascertain the conditions of experiment leading to the production of a maximum yield of metallic silver when ammoniacal solutions of certain silver compounds are reduced in the presence of aluminium and aqueous caustic alkali.

The reduction of silver oxide, prepared from silver nitrate, may be simply represented by the equations

(i) $6AgNO_3 + 6KOH = 3Ag_2O + 6KNO_3 + 3H_2O$,
(ii) $2Al + 6KOH = 2Al(OK)_3 + 3H_2$,
(iii) $3Ag_2O + 3H_2 = 6Ag + 3H_2O$,

one g.-atom of aluminium being equivalent to 3 g.-atoms of silver.

Preliminary experiments indicated that, in the absence of aluminium, heating of ammoniacal silver solutions in the presence of potassium hydroxide was followed by detonation. Addition of potassium hydroxide to concentrated solutions of silver compounds in aqueous ammonia caused the formation of black pre-

cipitates. Hydrolysis in the presence of traces of aluminium led to the detonation of such reaction mixtures. Hydrolysis of the dried black precipitates by potassium hydroxide gave silver oxide as the final product. In the presence of ammonia, spongy silver was formed. Analysis of the dried black precipitates by the Kjeldahl method showed that they were mixtures of silver nitride with relatively small quantities of silver oxide.

Experimental.

Series I.—An ammoniacal solution of silver nitrate containing 2 g. of the salt, 25 c.c. of ammonia (*d* 0·880), and 25 c.c. of water was treated with 25 c.c. of 3*N*-potassium hydroxide, and heated at 100° in a water-bath. At once a black film began to form on the walls of the reaction vessel, and its appearance was followed by an explosion which shattered the reaction vessel. This phenomenon occurred in three consecutive experiments, detonation taking place after a lapse of 12, 14, and 15 minutes from the commencement of the reaction.

Series II.—Aqueous silver nitrate solutions of various concentrations were treated with just sufficient ammonia (*d* 0·880) to redissolve the precipitated silver oxide, and to each solution were added 10 g. of potassium hydroxide dissolved in 15 c.c. of water. A brown precipitate formed; this was followed by a black precipitate as more caustic alkali was added. The final heavy precipitate was uniformly black in colour. The reaction vessel was then placed in a water-bath and heated to 100°. The black precipitate was thereby progressively reduced to a grey, metallic powder. The reduced metal was filtered, washed, dried, and analysed. In all cases, the filtrates were free from silver. Under the conditions of these experiments, it was observed that quantities of silver nitrate not exceeding 5 g. could be quantitatively reduced to metal. Attempts to reduce the silver salt in larger quantities invariably led to the explosion of the product. Typical results are given in Table I.

Table I.

Wt. of $AgNO_3$ (g.).....	0·5	1·0	2·0	3·0	4·0	5·0
% Ag ppd.	99·82	99·85	99·91	99·83	99·87	99·89
% Ag in ppt.	99·61	99·70	99·82	99·80	99·84	99·85

The conversion of the black precipitate into metallic silver was associated with the evolution of a gas, which was found to be nitrogen. The results of a quantitative examination of this reaction are summarised in the first two lines of Table II, and the last

lines show that the nitrogen evolved is chemically equivalent to the silver nitrate used. A similar result was obtained with silver chloride.

TABLE II.

Wt. of $AgNO_3$ (g.)	0·1619	0·2269	0·3176	0·4035	0·5892
Nitrogen (c.c. at *N.T.P.*)...	3·41	4·86	6·72	8·62	12·41
$AgNO_3$ (mg.-equiv.)	0·95	1·33	1·87	2·37	3·47
$\frac{1}{3}N$ (mg.-equiv.)	0·91	1·30	1·80	2·31	3·33

Series III.—Several samples of the black product were prepared as in Series II, 0·5 g. of silver nitrate being used in each case. Ordinary test-tubes were used as reaction vessels. One fragment of aluminium filings was quickly dropped into each reaction mixture, and the tubes were immediately immersed in vessels containing water at known temperatures. The observations were as follows:

(*a*) At 50°, crackling sound; (*b*) 60°, report; tube intact; (*c*) 70°, report, but louder; tube intact; (*d*) 90°, explosion; tube shattered; (*e*) 100°, violent explosion; tube shattered.

Analysis of the Black Precipitate.—A quantity of the black precipitate was prepared as in Series II. After 15 minutes, the supernatant liquor was decanted off, and the precipitate was washed by decantation with water and transferred to a filter. After thorough washing with water, the black precipitate was washed into a small tared evaporating dish, the excess of water evaporated on the water-bath, and the final drying completed by preserving over concentrated sulphuric acid. The product, which did not smell of ammonia, was then analysed. Owing to the great instability of the product, which exploded on percussion and even on touching with a spatula, it was deemed advisable to analyse it in bulk according to the following scheme:

(*a*) The black product was hydrolysed by means of strong caustic alkali, and the evolved ammonia estimated by absorption in standard sulphuric acid.

(*b*) The residual silver oxide was washed, dried, weighed, converted into nitrate, precipitated as chloride, and weighed in this form.

(*c*) The alkaline filtrate, from which the black product had been isolated, was examined for dissolved silver, which was precipitated and weighed as chloride. A typical result is given in Table III.

TABLE III.

Wt. of black ppt.	= 1·123 g.	$AgNO_3$ precipitated	= 85·13%
Nitrogen in ppt.	= 3·59%	$AgNO_3$ remaining in solution	= 15·03%
Ag in ppt.	= 95·48%		

From the above result, it would appear that the product was not homogeneous. In order to test this view the final, dry, black precipitate, prepared as above, was extracted several times with 50 c.c. of 10% ammonia solution. Analysis of the product after extraction and of the ammoniacal extract gave the following result.

TABLE IV.

Wt. of ppt. before extraction	= 1·132 g.	% of total $AgNO_3$ ppd.	= 84·68
Wt. of ppt. after extraction	= 0·989 g.	% of $AgNO_3$ in extract	= 10·33
Nitrogen in ppt.	= 4·11%	% of $AgNO_3$ in solution	= 15·19
Silver in ppt.	= 95·50%		

From a series of experiments, it was ascertained that a similar black precipitate containing nitrogen could be obtained when silver chloride was used instead of silver nitrate.

Series IV.—Reduction at 100°, *in ammoniacal solution, using varying quantities of aluminium and definite amounts of dissolved silver in the presence of potassium hydroxide.* The required quantity of the silver compound, containing silver equivalent to that present in 2 g. of the nitrate, was treated in an ammoniacal solution, containing 25 c.c. of ammonia (*d* 0·880) and 25 c.c. of water, with 25 c.c. of 3*N*-potassium hydroxide. A definite quantity of aluminium filings was then added and the reduction carried out at 100°; a black product was deposited, the colour of which changed rapidly to grey; from this stage onwards the quantity of the reduced metal increased continuously throughout the experiment. The final product formed grey, coherent masses of reduced silver possessing a vesicular structure. The reduction was complete in 1½ hours, and the reaction liquid was then treated with 10 c.c. of ammonia (*d* 0·880), allowed to stand for 15 minutes with frequent shaking, diluted with half its bulk of distilled water, and filtered through a tared Gooch crucible. The reduced silver was thoroughly washed, dried at 100°, weighed, and analysed. The results for silver nitrate are given in Table V, and those for silver oxide and silver chloride were very similar.

TABLE V.

Al used (g.)	0·05	0·10	0·20
Ag ppd., %	99·88	99·82	99·79
Ag in ppt., %	99·83	99·89	99·87

Series V.—A solution was prepared exactly as in Series IV, a strip of sheet aluminium was placed in it, and, immediately, a black deposit formed on the surface of the metal. After 30 seconds, the strip was removed, the deposit transferred to a beaker by means of a jet of water, and the strip reimmersed in the silver solution. This was repeated (10 times) until the deposit had

obtained in a quantity sufficient for analysis, which showed it to be elementary silver.

Series VI.—Ammoniacal solutions of silver nitrate were prepared, the ammonia content being just sufficient to retain the silver in solution. 2 C.c. of ammonia (*d* 0·880) were added, *i.e.*, excess sufficient to prevent the formation of black precipitates (total maximum bulk, 10 c.c.). Each solution was treated with 2 g. of potassium hydroxide dissolved in 5 c.c. of water, the required quantity of aluminium added, and the dissolved silver submitted to reduction at 100°. The volume of gas evolved was determined, and the gas proved to be nitrogen. Typical results are given in Table VI.

TABLE VI.

Wt. of Al (g.)	0·01	0·01	0·01	0·02	0·03
Wt. of $AgNO_3$ (g.)	0·2884	0·5378	0·7500	0·7500	0·7500
Nitrogen (c.c. at *N.T.P.*)	1·92	7·33	11·97	7·89	3·78
% Ag ppd.	99·52	99·81	99·82	99·88	99·84

It was observed that the evolution of nitrogen was retarded.

The results obtained indicate that the amount of silver reduced is stoicheiometrically equal to the aluminium dissolved *plus* the nitrogen evolved, *i.e.*, that Ag^+ reduced = Al oxidised + NH_3 oxidised, thus (in mg.-equivs.):

⅓Al	1·1	1·1	1·1	2·2	3·3
⅓N	0·5	2·0	3·2	2·1	1·0
Sum	1·6	3·1	4·3	4·3	4·3
$AgNO_3$	1·7	3·2	4·4	4·4	4·4

Series VII.—Reduction at 100°, *in ammoniacal solution, using a fixed quantity of aluminium, and varying amounts of dissolved silver in the presence of potassium hydroxide.* The object of this series was to ascertain the maximum effect of a definite quantity of aluminium under given conditions of experiment. 0·05 G. of aluminium was used in each case. The bulk of the mixed solutions and the concentration of ammonia were similar to those of Series IV. The quantities of silver compound used were equivalent to 2—8 g. of nitrate. In all experiments up to a silver content equivalent to 6 g. of nitrate, a quantitative yield of silver was obtained. The use of more concentrated solutions of silver frequently resulted in explosions. In this series it was observed that the first-formed, coherent masses of silver gradually changed to a granular powder. The results are given in Table VII.

TABLE VII.

Wt. of Ag compd. (g.) ...	2	3	4	5	6
Wt. of Ag ppd. (g.)	1·27	1·90	2·54	3·17	3·80
% Ag ppd.	99·73	99·82	99·79	99·83	99·89
% Ag in ppt.	99·79	99·88	99·85	99·80	99·84

Series VIII.—Reduction at 100°, *in ammoniacal solution, using definite quantities of aluminium in the presence of potassium hydroxide, the solutions of silver used during the process of reduction being added from time to time in measured volumes of known ammonia and silver content.* From the preceding series it seemed probable that the concentration of the silver salt relative to the ammonia content of the alkaline solution employed is a factor governing the stability of the ammoniacal solutions submitted to reduction. The present series was carried out to test this view.

A solution containing 2 g. of silver salt, prepared as in Series IV, was treated with 0·05 g. of aluminium filings. An additional series of solutions was prepared containing 2 g. of the same silver salt in 25 c.c. of ammonia (*d* 0·880) and 25 c.c. of water. At the end of consecutive intervals of 20 minutes, these solutions were, in turn, added to the reaction liquid undergoing reduction. The total quantity of silver salt thus added was equivalent to 8 g. of the silver salt employed. The resulting reduced silver formed grey, coherent masses. The results are given in Table VIII.

TABLE VIII.

	From $AgNO_3$.	From AgCl.
Wt. of ppt. (g.)	4·26	3·64
% Ag in ppt.	99·89	99·85
% Ag ppd.	66·94	48·27

Series IX.—As in Series VIII, activated silver being used instead of aluminium filings. Quantities of reduced silver, prepared as in Series IV, were activated by heating in a vacuum in a quartz tube for 3 hours at 900°, the samples of the metal obtained from the different salts being submitted to heat treatment separately. The method of experiment was as in Series VIII. The total quantity of silver salt added was equivalent to 8 g. of the silver salt used. Two series of experiments were carried out on activated silver from (i) silver nitrate, and (ii) cf. silver chloride. Table IX contains the results for the first series.

TABLE IX.

Activated Ag used (g.).	$AgNO_3$.			AgCl.		
	Wt. of ppt. (g.).	% Ag in ppt.	% Ag ppd.	Wt. of ppt. (g.).	% Ag in ppt.	% Ag ppd.
0·4	2·54	99·89	39·91	1·96	99·87	26·05
0·6	3·11	99·92	48·89	2·73	99·90	36·29
0·8	3·61	99·87	56·80	2·81	99·88	37·42
1·0	3·95	99·84	62·15	3·08	99·85	40·82

Discussion and Conclusions.

Under the conditions of experiment for hydrolysis at 100°, the black precipitates are transformed to metallic silver, while the

reaction liquids are found to be free from dissolved silver. In so far as the black precipitates are unstable in the presence of traces of aluminium, it would seem that deposition of silver nitride, prior to the final separation of metallic silver, is entirely inhibited with respect to the different processes of reduction which proceed without detonation of the reaction mixture.

In the absence of aluminium, the different amounts of dissolved silver quantitatively separated as reduced metal are equivalent to the volumes of nitrogen evolved. In the presence of aluminium, the evolution of nitrogen is inhibited : the formation of this gas does not commence until every trace of metallic aluminium has been dissolved as aluminate.

The quantitative yields of reduced silver obtained under conditions for the production of nitrogen in presence of aluminium would appear, therefore, to be the cumulative effect of two distinct reactions. In the first reaction, metallic silver is separated from the solution in a quantity equivalent to the amount of aluminium employed. The newly deposited silver, being in a finely divided condition, serves to stabilise the ammoniacal solution containing the remainder of the silver present in the dissolved state, and, as in the experiments involving the employment of activated silver (compare Series IX), it imparts to the silver solution the increment of energy necessary for the commencement of the second reaction. The second reaction then proceeds to completion, the deposition of silver being accompanied by the evolution of nitrogen in the proportion of 3 atoms of silver to 1 atom of nitrogen.

It would seem, therefore, that, in the presence of ammonia, caustic alkali effects precipitation of silver nitride, with small amounts of silver oxide, through the formation of an intermediate complex, $(NH_3)_2AgOH$, according to the following equations :

$$\text{(Ai)}\quad (NH_3)_2AgNO_3 + KOH = (NH_3)_2AgOH + KNO_3,$$
$$\text{(Aii)}\quad (NH_3)_2AgCl + KOH = (NH_3)_2AgOH + KCl,$$
$$\text{(B)}\quad 3(NH_3)_2AgOH + 2H_2O = 5NH_4OH + NAg_3,$$
$$\text{(C)}\quad 2(NH_3)_2AgOH + 3H_2O = 4NH_4OH + Ag_2O$$

(compare Bodländer and Fittig, *Z. physikal. Chem.*, 1902, **39**, 597; Straub, *ibid.*, 1911, **77**, 331).

At 100° the reactions represented by (B) and (C) are suppressed, decomposition of the diamminoargentic complex, evolution of nitrogen, and separation of silver taking place according to the equation

$$\text{(D)}\quad 6(NH_3)_2AgOH + 4H_2O = 6Ag + N_2 + 10NH_4OH.$$

It is concluded that the first reaction takes place, in the presence of aluminium, accompanied by changes conveniently represented

by the equations given on p. 1772. The second reaction involves transformations represented by the equations (Ai or Aii), (B), (C), and (D).

The results of Series IV and VII show that the extent of reduction is determined by the conditions of experiment. Thus, in Series VII, 6 g. of silver nitrate in 75 c.c. of reaction solution are completely reduced by the introduction of 0·05 g. of aluminium. By the modifications introduced in Series VIII larger quantities can be reduced without explosion, and 0·05 g. of aluminium reduces 6·694 g. of silver nitrate or 4·827 g. of silver chloride.

Series IX shows that, in absence of aluminium, ammoniacal solutions of silver nitrate or silver chloride may be reduced by means of freshly reduced silver from Series IV, activated by heating in a vacuum for 3 hours at 900°, 1 g. of activated silver being capable of reducing 6·215 g. or 4·082 g. of silver nitrate or chloride, respectively.

The continuous separation of finely divided silver in the form of grey, coherent masses possessing a vesicular structure is constantly exposing an ever-increasing surface of metal to the ammoniacal solution undergoing reduction. Uninterrupted contact between the surface of the newly deposited metal and the solution induces energy changes involving decay in the activity of the reduced metal followed by the separation of further quantities of silver from the solution. Prolonged contact between the reduced metal and the solution ultimately brings about a marked decay in the activity of the reduced metal, and this change is accompanied by the following characteristic effects. The coherent masses of reduced metal gradually break down to a powder, whilst the continued isolation of silver from the solution is ultimately brought to a limit beyond which no further appreciable deposition of reduced metal takes place.

In the presence of relatively large amounts of ammonia, separation of silver from ammoniacal silver solutions can be effected only when a suitable source of energy is introduced into the reacting system. Under given conditions of experiment, aluminium, in the presence of aqueous caustic alkali, may be employed to induce and control the production of reduced silver. When the ammoniacal concentration of the solution undergoing reduction has fallen to a certain limiting value, the concentration of the dissolved silver rises to a value such that it is unnecessary to supply energy to the reacting system: the residual ammonia is then unable to control the reaction, whilst the external heat applied in order to maintain the temperature of the reaction becomes more than sufficient to supply the energy necessary to allow the reaction to continue.

the result that the reaction is accelerated, and ultimately proceeds with explosive velocity. In these circumstances, therefore, the employment of aluminium, in the presence of caustic alkali, is quite unnecessary, and can lead only to an increase in the intensity of the explosive effects observed (compare Baly, *Ann. Report*, 1921, **18**, 40).

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April 8th*, 1927.]

CCXXXIII.—*Molecular Volumes at Absolute Zero. Part I. Density as a Function of Temperature.*

By SAMUEL SUGDEN.

DURING the last few years it has been shown by the author and others that there are several empirical relations between surface tension, density, and temperature which hold with considerable accuracy over a large range of the variables concerned. Of these, the most important for the present discussion are van der Waals's equation (*Z. physikal. Chem.*, 1894, **13**, 716) for the variation of surface tension with temperature,

$$\gamma = \gamma_0(1 - T_r)^{6/5} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and Macleod's relation (*Trans. Faraday Soc.*, 1923, **19**, 38) between surface tension and density,

$$\gamma = C(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In these equations, γ is the surface tension, T_r the reduced temperature, D and d are the densities of the liquid and saturated vapour, respectively, and γ_0 and C are constants.

The first equation has been shown to give the experimental values of the surface tension of non-associated liquids from the ordinary temperature to within a few degrees of the critical point (Sugden, J., 1924, **125**, 32). Equation (2) was shown by the present author to hold for a large number of liquids over a wide range of temperatures. Further, from this equation is derived the formula for calculating the parachor $[P]$ where

$$[P] = MC^{1/4} = M\gamma^{1/4}/(D - d) \quad . \quad . \quad . \quad . \quad (3)$$

(M = molecular weight). This constant is found to be an accurately additive function of certain atomic and structural constants (Sugden, J., 1924, **125**, 1177; Sugden, Reed, and Wilkins, J., 1925, **127**, 1525; Sugden and Whittaker, *ibid.*, p. 1868; Sugden and Wilkins,

ibid., p. 2517; this vol., p. 139), and in particular provides a clear experimental distinction between non-polar and semipolar double bonds.

These two equations, although empirical and at present not related to any theory of the liquid state, are supported by a considerable amount of experimental evidence. From them, it is obviously possible to deduce a number of other relationships between the variables concerned, including a modified form of the Ramsay-Shields equation (compare Ferguson, *Trans. Faraday Soc.*, 1923, **19**, 41, 407). The simplest of these is a relation between density and temperature

$$D - d = D_0(1 - T_r)^{3/10} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is obtained by eliminating γ between equations (1) and (2). Abundant material for testing this equation is to be found in the data of Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374), which include measurements of the liquid and vapour densities of 30 substances. For all of them equation (4) is found to hold with remarkable accuracy; to save space, however, the calculations will only be given for the liquids to which equation (1) has been applied in a previous communication.

Equation (4) contains two constants, D_0 and the critical temperature, since $T_r = T/T_c$. These were determined by calculating the value of $(D - d)^{10/3}$ at intervals of 40°, since this quantity is a linear function of temperature, and applying the method of "zero sum" (Campbell, *Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816). The constants obtained in this manner were then used to calculate the density difference $(D - d)$ at each temperature; the results are shown in Table I, from which it will be seen that equation (4) reproduces the experimental data with a high degree of accuracy—in general the difference between the observed and the calculated values of $D - d$ is 1 part in 500 parts. A few greater deviations are found in the neighbourhood of the critical point, but in this region it is difficult to measure the density of the saturated vapour with precision.

The six liquids named in Table I belong to the class of unassociated liquids. Table II gives similar data for two associated liquids, *viz.*, acetic acid and ethyl alcohol, and shows that equation (4) holds for a part of the range; above a definite temperature, however, the density decreases more rapidly than is indicated by the formula, and the critical point is reached at a lower temperature than would be expected from the slope of the density–temperature curve at low temperatures. This effect is scarcely appreciable for acetic acid, but more pronounced for ethyl alcohol. It would seem, therefore, that association has little or no influence on the density, provided

TABLE I.

Variation of Density with Temperature.

Benzene.

t.	$D-d$ (obs.).	$D-d$ (calc.).	Diff.
0°	0·9000	0·8968	−0·0032
40	0·8568	0·8571	+0·0003
80	0·8118	0·8126	+0·0008
120	0·7615	0·7615	±0·0000
160	0·7012	0·7008	−0·0004
200	0·6250	0·6246	−0·0004
240	0·5137	0·5169	+0·0032
280	0·2854	0·2743	−0·0111

t_c (obs.), 288·5.

Chlorobenzene.

$D-d$ (obs.).	$D-d$ (calc.).	Diff.
1·1279	1·1237	−0·0042
1·0844	1·0845	+0·0001
1·0411	1·0420	+0·0009
0·9934	0·9944	+0·0010
0·9412	0·9416	+0·0004
0·8804	0·8795	−0·0009
0·8056	0·8057	+0·0001
0·7342	0·7378	+0·0036 (270°)

t_c (obs.), 359·2.

Ethyl ether.

0°	0·7354	0·7368	+0·0014
40	0·6857	0·6866	+0·0009
80	0·6286	0·6260	−0·0026
120	0·5471	0·5475	+0·0004
160	0·4256	0·4270	+0·0014
180	0·3133	0·3129	−0·0004

t_c (obs.), 193·8.

Methyl formate.

1·0025	1·0030	+0·0005
0·9415	0·9416	+0·0001
0·8698	0·8692	−0·0006
0·7801	0·7793	−0·0008
0·6513	0·6550	+0·0037
0·4134	0·4134	±0·0000 (200°)

t_c (obs.), 214.

Ethyl acetate.

0°	0·9243	0·9235	−0·0008
40	0·8754	0·8760	+0·0006
80	0·8210	0·8217	+0·0007
120	0·7580	0·7571	−0·0009
160	0·6775	0·6767	−0·0008
200	0·5630	0·5641	+0·0011
240	0·3279	0·3296	+0·0017

t_c (obs.), 250·1.

Carbon tetrachloride.

1·6323	1·6301	−0·0022
1·5540	1·5558	+0·0018
1·4704	1·4722	+0·0018
1·3738	1·3758	+0·0020
1·2617	1·2605	−0·0012
1·1146	1·1134	−0·0012
0·8980	0·8973	−0·0007

t_c (obs.), 283·15.

that the degree of association does not change with temperature. This conclusion is supported by the fact that the value of D_0 found for acetic acid is almost identical with that for its isomeride methyl formate, whilst the values for the alcohols, as will be shown in the following paper, are those to be expected from their composition.

TABLE II.

Variation of Density with Temperature. (Associated liquids.)

Acetic acid.

t.	$D-d$ (obs.).	$D-d$ (calc.).	Diff.
0°	1·0697	1·0700	+0·0003
40	1·0282	1·0288	+0·0006
80	0·9825	0·9826	+0·0001
120	0·9329	0·9315	−0·0014
160	0·8740	0·8722	−0·0018
200	0·8060	0·8020	−0·0040
240	0·7138	0·7136	−0·0002
280	0·5746	0·5878	+0·0132

t_c (obs.), 321·6.

Ethyl alcohol.

$D-d$ (obs.).	$D-d$ (calc.).	Diff.
0·8065	0·8070	+0·0005
0·7719	0·7720	+0·0001
0·7331	0·7326	−0·0005
0·6859	0·6876	+0·0017
0·6137	0·6344	+0·0207
0·5060	0·5682	+0·0522
0·2110	0·4764	+0·2654
—	—	—

t_c (obs.), 243·1.

The critical temperatures predicted from the density observations are collected in Table III and are compared with the observed values and also with the values deduced from the variation of surface tension with density (Sugden, J., 1924, **125**, 32). It will be seen that, in general, the unassociated liquids give a good agreement between the observed and the calculated critical temperatures, whilst for associated liquids the observed critical temperature is markedly lower than that predicted from the lower part of the density curve.

TABLE III.

Substance.	Critical temperature from density.	Critical temperature from surface tension.	Critical temperature obs.
Benzene	285·5°	287°	288·5°
Chlorobenzene	358	358	359·2
Ethyl ether	191	193	193·8
Methyl formate	211	212	214
Ethyl acetate	248	249	250·1
Carbon tetrachloride	278	280	283·1
Methyl alcohol	279	—	240
Ethyl alcohol	290	—	243·1
Acetic acid	324	—	321·6

Since equation (4) represents the variation of density with temperature with great precision as the temperature increases, it is reasonable to suppose that it will also hold as the temperature decreases. The constant D_0 is therefore of considerable interest, since it represents the density of the supercooled liquid at absolute zero. The values of this constant are collected in Table IV, and if

TABLE IV.

Zero Volumes and the Parachor.

Substance.	D_0.	V_0.	$[P]$.	$[P]/V_0$.
Benzene	1·0965	71·2	207·1	2·91
Chlorobenzene	1·3323	84·4	244·3	2·89
Ethyl ether	0·9616	77·1	210·0	2·73
Methyl formate	1·2863	46·7	138·0	2·96
Ethyl acetate	1·1538	76·4	216·0	2·83
Carbon tetrachloride	2·0015	77·4	222·0	2·87
Methyl alcohol	0·9936	32·3	93·2*	2·89
Ethyl alcohol	0·9846	46·8	132·2*	2·82
Acetic acid	1·2853	46·7	138·0*	2·96

* Calculated from the atomic and structural constants.

these numbers are divided into the molecular weight of the liquid, the molecular volume (V_0) at absolute zero is obtained: this will be referred to as the "zero volume." The column headed $[P]$ gives the calculated value of the parachor for each liquid, and the fifth column shows that the ratio $[P]/V_0$ is nearly constant for the nine

substances tabulated. This constancy must, however, be regarded as fortuitous, since from equations 1, 3, and 4 it is readily shown that

$$[P] = \gamma_0^{1/4} V_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For organic substances γ_0 has values ranging from about 60 to 80, so the fourth root of this, which gives the ratio $[P]/V_0$, does not vary much. If, however, the range is extended on the one hand to hydrogen, which has a small value of γ_0, and on the other hand to metals and their salts, which have large surface tensions, it is found that the zero volume is no longer proportional to the parachor.

A relation of greater significance is exhibited in Table V, which shows that the zero volume is very nearly a constant fraction of the critical volume. The data for hydrogen are given by Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 528), and those for the other substances by Young (*loc. cit.*). Except in the case of hydrogen the ratio V_0/V_c is very nearly constant over the whole range considered.

TABLE V.

Zero Volumes and Critical Volumes.

Substance.	V_0.	V_c.	V_0/V_c.
Hydrogen	22·0	46·9	0·373
Ethyl ether	77·1	281·9	0·273
Carbon tetrachloride	77·4	276·1	0·280
Methyl formate	46·7	172·0	0·271
Methyl acetate	61·1	227·8	0·268
Methyl propionate	75·5	282·0	0·268
Ethyl acetate	76·4	286·3	0·267
Propyl formate	76·7	284·8	0·269
Methyl butyrate	90·7	340·1	0·267
Methyl *iso*butyrate	90·6	335·9	0·267
Ethyl propionate	90·9	344·3	0·264
Propyl acetate	91·3	345·3	0·264
n-Pentane	83·9	310·3	0·270
*iso*Pentane	86·1	307·0	0·280
Di*iso*propyl	99·9	357·3	0·280
n-Heptane	114·9	427·1	0·269
n-Octane	130·8	490·7	0·267
Di*iso*butyl	116·7	417·5	0·280
Benzene	71·2	256·1	0·278
Fluorobenzene	75·1	271·2	0·277
Chlorobenzene	84·4	307·8	0·274
Bromobenzene	88·3	323·5	0·273

Formulæ of the type of equation (1) have been suggested by earlier workers. Thus van der Waals (*Z. physikal. Chem.*, 1894, **13**, 695) gave the equation

$$V - v = mV_c(1 - T_r)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

based on the theory of corresponding states. Here V and v are the specific volumes of vapour and liquid, respectively. Verschaffelt

(Commun. of Leiden, No. 28, 1896) advanced the general formula

$$D - d = mD_c(1 - T_r)^n \quad . \quad . \quad . \quad . \quad . \quad (6)$$

making $n = 0{\cdot}367$ for carbon dioxide. Goldhammer (*Z. physikal. Chem.*, 1910, **71**, 577) tested this formula on Young's density data, using $n = 1/3$ with fairly satisfactory results. It is readily shown that the exponent 3/10 gives results in better agreement with the available data than does Goldhammer's exponent 1/3, for $(D - d)^{10/3}$ is a linear function of temperature (see Table VI), as it should be according to equation (4), whereas $(D - d)^3$ exhibits a temperature coefficient which definitely increases with rise of temperature.

TABLE VI.

t.	$D-d$.	$(D-d)^{10/3}$.	Temp. coeff. $\times 10^5$.	$(D-d)^3$.	Temp. coeff. $\times 10^5$.
			Ether.		
0°	0·7354	0·3589		0·3976	
			186		185
40	0·6857	0·2844		0·3237	
			179		188
80	0·6286	0·2129		0·2484	
			197		212
120	0·5471	0·1340		0·1638	
			190		216
160	0·4256	0·0580		0·0771	
			186		231
180	0·3133	0·0209		0·0308	
			Ethyl acetate.		
0°	0·9243	0·7691		0·7896	
			319		297
40	0·8754	0·6416		0·6709	
			309		294
80	0·8210	0·5180		0·5532	
			302		294
120	0·7580	0·3972		0·4356	
			310		312
160	0·6775	0·2730		0·3109	
			314		331
200	0·5630	0·1473		0·1785	
			308		358
240	0·3279	0·0243		0·0353	

Summary.

1. The variation of density with temperature from the freezing point to the critical point is represented accurately for normal liquids by the equation $D - d = D_0(1 - T/T_c)^{3/10}$, where D and d are the densities of the liquid and saturated vapour, respectively, at $T°$ Abs.

2. This equation also holds for associated liquids over the lower part of the temperature range, and in some cases nearly to the critical point.

3. The "zero volume," V_0, obtained by dividing the molecular weight by the constant D_0, is nearly proportional to the critical volume for a large number of substances.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4.

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CCXXXIV.—*Molecular Volumes at Absolute Zero. Part II. Zero Volumes and Chemical Composition.*

By SAMUEL SUGDEN.

IT has been shown (preceding paper) that the influence of temperature on the density of a liquid is represented accurately by the equation

$$D - d = D_0(1 - T/T_c)^{3/10} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D and d are the densities of the liquid and its saturated vapour, respectively, at a temperature T, and T_c is the critical temperature. The constant D_0 is the density the liquid would have at absolute zero if equation (1) still held; this assumption is probably not far from the truth, since the coefficient of expansion decreases continually as the temperature falls and is already small at the freezing point. In general, equation (1) gives values for D_0 which are about 20% greater than the density at 0°, so that if sufficiently accurate density data over a wide range of temperatures are available, the extrapolation seems to be justifiable.

By dividing this constant into the molecular weight one obtains the "zero volume," V_0, *i.e.*, the molecular volume of a supercooled liquid at absolute zero; this appears to be a very significant constant, for the form of equation (1) shows that zero volumes are proportional to the molecular volumes for a series of liquids at the same reduced temperature, *i.e.*, they are corresponding volumes. It has also been shown in Part I that zero volumes are nearly proportional to critical volumes in a number of cases in which the latter constant has been determined with accuracy.

It will now be shown that zero volumes are an additive function of chemical composition, and can be predicted with considerable accuracy for a large number of substances by adding together suitable constants for the atoms and structures present in the molecule. In the tables, the zero volumes of 284 substances are recorded and compared with the values obtained by adding the constants given in Table II. For 236 substances, or 82% of the number studied, the difference between the extrapolated and the calculated values does not exceed 2%.

The method by which D_0 is calculated from a range of density observations is outlined in Part I (p. 1781). It is obvious that the accuracy of the value found will depend on the accuracy and temperature range of the data employed. For most of the substances studied, densities accurate to 1 part in 1000 parts over a range of 40° or more have been used, and it is estimated that the maximum error in the calculation of D_0 is considerably less than ½%. In a

few cases, the available observations covered a smaller temperature range, and the values of V_0 found may therefore be burdened with a larger error of calculation; these are indicated in the tables by parentheses.

(2) *Evaluation of Constants.*

The first evidence that zero volumes are simply related to chemical composition is given by the fact that position isomerides give nearly the same value for this constant. Some examples are quoted in Table I, and others will be found in the tables which follow.

TABLE I.

Position Isomerides.

$C_2H_4O_2$.	V_0.	C_8H_{10}.	V_0.
Methyl formate	46·7	Ethylbenzene	(99·3)
Acetic acid	46·7	*o*-Xylene	(98·9)
		m- ,, ...	(99·1)
$C_9H_{18}O_2$.		*p*- ,, ...	(100·7)
Ethyl *n*-heptoate	149·6	$C_8H_{10}O$.	
d-β-Butyl *n*-valerate	150·8	Phenetole	105·5
d-β-Hexyl propionate	149·7	*m*-Tolyl methyl ether	(103·9)
d-β-Heptyl acetate	150·5	*p*- ,, ,, ,, ...	(104·0)

It was next found that several homologous series (hydrocarbons, alkyl halides, ethers, esters, ketones, aldehydes, and amines) gave very nearly a constant difference in zero volumes for a difference in composition of CH_2; the values found for this constant ranged from 14·2 to 14·9 in different series with a weighted mean of $CH_2 = 14·5$. From this value, the constant for hydrogen was obtained by subtracting nCH_2 from a series of observations for the paraffins C_nH_{2n+2}, the mean value being H = 6·7, whence C = 1·1. These fundamental constants were then employed to evaluate the constants for other elements and structures.

It soon became apparent that the analysis of zero volumes could be carried out with the same simplicity as is met with in the case of the parachors (Sugden, J., 1924, **125**, 1177). With one or two exceptions (see p. 1796), the same constant serves for a particular atom in all its compounds, and the same constant for a particular structure, no matter what elements are taking part in it. Thus a double bond has the same value in ethylene derivatives, ketones, esters, and benzene derivatives; the last can all be expressed satisfactorily on the basis of the Kekulé formula. The most probable values for a number of atomic and structural constants are collected in Table II.

A clear distinction is also shown between the two types of double bond which have already been differentiated by means of the parachor (Sugden, Reed, and Wilkins, J., 1925, 127, 1525).

TABLE II.

Atomic and Structural Constants.

Atomic constants.		Atomic constants.		Structural constants.	
H	= 6·7	I	= 28·3	Triple bond	= 15·5
C	= 1·1	P	= 12·7	Double bond	= 8·0
N	= 3·6	S	= 14·3	3-Membered ring	= 4·8
O	= 5·0	O (in alcohols)	= 3·0	4-Membered ring	= 3·2
F	= 10·3	N (in amines)	= 0·0	5-Membered ring	= 1·8
Cl	= 19·3			6-Membered ring	= 0·6
Br	= 22·1			Semipolar double bond	= 0·0

is demonstrated by the data in Table III, in which the column headed ΣV_0 gives the sum of the atomic and structural constants for the substance considered except that for the linkage to be determined. By subtracting ΣV_0 from V_0 (obs.) the value shown in the last column for each type of double bond is obtained. It will be seen that, whilst a non-polar double bond gives a nearly constant increase of 8·0 c.c. in the zero volume, a semipolar double bond gives a constant which fluctuates about a value of zero.

TABLE III.

(i) Non-polar double bonds.

Substance.	Formula.	V_0 (obs.).	ΣV_0.	Double bond.
Ethylene	C_2H_4	37·4	29·0	8·4
Propylene	C_3H_6	51·7	43·5	8·2
Benzene	C_6H_6	71·2	47·4	7·9×3
Toluene	C_7H_8	86·7	61·9	8·3×3
Acetone	C_3H_6O	56·0	48·5	7·5
Acetylacetone	$C_5H_8O_2$	84·5	69·1	7·7×2
Methyl formate	$C_2H_4O_2$	56·7	39·0	7·7
Ethyl acetate	$C_4H_8O_2$	76·4	68·0	8·4

(ii) Semipolar double bonds.

Thionyl chloride	$SOCl_2$	58·0	58·1	−0·1
Sulphuryl chloride	SO_2Cl_2	62·6	63·1	−0·25×2
Methyl sulphate	$C_2H_6SO_4$	78·5	75·9	+1·3×2
Ethyl sulphite	$C_4H_{10}SO_3$	101·1	100·9	+0·2
Ethyl ethanesulphonate	"	96·7	"	−2·1×2
Ethyl sulphate	$C_4H_{10}SO_4$	107·3	103·9	+1·7×2
Nitrobenzene	$C_6H_5NO_2$	87·0	85·8	+1·2
Phosphorus oxychloride	$POCl_3$	73·4	75·4	−2·0
Ethyl phosphate	$C_6H_{15}PO_4$	140·5	139·6	+0·9
Phenyl phosphate	$C_{18}H_{15}PO_4$	(230·2)	226·8	+3·4
Nitric acid	HNO_3	32·7	33·3	−0·6
Sulphuric acid	H_2SO_4	47·1	47·7	−0·3×2
Perchloric acid	$HClO_4$	45·7	46·0	−0·1×3

It is noteworthy that the existence of the two types of double bond is now demonstrated by three independent lines of experimental evidence: (1) The different effect produced by these linkages on the parachor (Sugden, Reed, and Wilkins, *loc. cit.*), (2) the evidence from the optical activity of certain sulphur compounds which contain semipolar double bonds (Phillips, J., 1925,

127, 2552; 1926, 2079; this vol., p. 188), and (3) the effect of these two linkages upon the zero volume. The last of these methods has the advantage that it is applicable to associated liquids and shows (compare Table III) that free nitric, sulphuric, and perchloric acids contain, respectively, one, two, and three semipolar double bonds in accordance with the requirements of the octet theory of valency.

(3) *Normal Liquids.*

In this and the following section a comparison is made between the values of V_0 (obs.) derived from the density data and the predicted figure, V_0 (calc.), obtained by adding together the constants recorded in Table II. The column headed "Observer" gives initials only; full references are given on p. 1797.

Table IV gives the data for hydrocarbons.

TABLE IV.

Hydrocarbons.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
1. Acetylene	C_2H_2	M. & W.	31·6	31·1	−1·6
„	„	Math.	32·0	„	−2·8
2. Ethylene	C_2H_4	M. & W.	37·4	37·0	−1·1
3. Ethane	C_2H_6	„	41·4	42·4	+2·4
4. Allylene	C_3H_4	„	44·3	45·6	+2·9
5. Propylene	C_3H_6	„	51·7	51·5	−0·4
6. Propane	C_3H_8	„	56·2	56·9	+1·3
7. *n*-Butane	C_4H_{10}	Wiss.	69·6	71·4	−2·6
8. *n*-Pentane	C_5H_{12}	Y.	83·9	85·9	+2·4
9. *iso*Pentane	„	„	86·1	„	−0·2
10. Benzene	C_6H_6	„	71·2	71·4	+0·3
„	„	P.	70·6	„	+1·2
11. Methyl*cyclo*pentane	C_6H_{12}	K.	(88·3)	88·8	+0·6
12. *cyclo*Hexane	„	J.	86·7	87·6	+1·0
„	„	Y.	86·0	„	+1·8
13. *n*-Hexane	C_6H_{14}	„	100·8	100·4	−0·4
14. Di*iso*propyl	„	„	99·9	„	+0·5
15. Toluene	C_7H_8	„	86·7	85·9	−0·9
„	„	P.	86·2	„	−0·3
16. Methyl*cyclo*hexane	C_7H_{14}	K.	102·6	102·1	−0·5
17. *n*-Heptane	C_7H_{16}	Y.	115·7	114·9	−0·7
„	„	P.	116·2	„	−1·2
18. Ethylbenzene	C_8H_{10}	„	(99·3)	100·4	+1·1
19. *o*-Xylene	„	„	(98·9)	„	+1·5
20. *m*- „	„	„	(99·1)	„	+1·3
21. *p*- „	„	„	(100·7)	„	−0·3
22. 1 : 1-Dimethyl*cyclo*hexane	C_8H_{16}	K.	(117·4)	116·6	−0·7
23. *n*-Octane	C_8H_{18}	Y.	130·8	129·4	−1·0
24. Di*iso*butyl	„	„	130·9	„	−1·1
25. *p*-Cumene	C_9H_{12}	P.	113·4	114·9	+1·4
26. Cumene	„	„	(113·8)	„	+1·0
27. Mesitylene	C_9H_{12}	P.	115·0	114·9	−0·1
28. *n*-Propylbenzene	„	„	(113·8)	„	+1·0
29. *p*-Cymene	$C_{10}H_{14}$	„	(128·6)	129·4	+0·7
30. *iso*Butylbenzene	„	„	(128·8)	„	+0·5

It may be noted that the densities of di*iso*butyl quoted by Landolt–Bornstein (4th edn., 1912, p. 154) are wrongly transcribed from Young's paper; the figures given are the densities of *cyclo*hexane which appear on the adjoining page.

Tables V, VI, VII, and VIII are self-explanatory. Some marked

TABLE V.

Halogen Derivatives.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
31.	Carbon tetrachloride	CCl_4	Y.	77·4	78·3	+1·2
32.	Methylene iodide	CH_2I_2	P.	68·4	71·1	+3·9
33.	Acetylene tetrachloride	$C_2H_2Cl_4$	J.	87·7	92·8	+5·8
34.	„ tetrabromide	$C_2H_2Br_4$	„	100·9	104·0	+3·1
35.	Ethylene dichloride	$C_2H_4Cl_2$	„	62·8	67·6	+7·7
	„ „	„	P.	62·8	„	+7·7
36.	Ethyl iodide	C_2H_5I	„	64·2	64·0	−0·3
37.	*n*-Propyl bromide	C_3H_7Br	„	71·6	72·3	+1·0
38.	*p*-Dichlorobenzene	$C_6H_4Cl_2$	„	96·8	96·6	−0·2
39.	Fluorobenzene	C_6H_5F	Y.	75·1	75·0	−0·1
40.	Chlorobenzene	C_6H_5Cl	„	84·4	84·0	−0·4
	„	„	P.	83·2	„	+1·0
41.	Bromobenzene	C_6H_5Br	„	87·9	86·8	−1·3
	„	„	Y.	88·3	„	−1·7
42.	Iodobenzene	C_6H_5I	„	95·5	93·0	−2·6
	„	„	P.	94·1	„	−1·2
43.	*p*-Fluorobromobenzene	C_6H_4FBr	J.	90·8	90·4	−0·4
44.	*p*-Chlorobromobenzene	C_6H_4ClBr	S.	99·1	99·4	+0·3
45.	*p*-Chloroiodobenzene	C_6H_4ClI	„	102·9	105·6	+2·6
46.	*m*-Fluorotoluene	C_7H_7F	J.	90·2	89·5	−0·8
47.	*p*-Bromotoluene	C_7H_7Br	P.	102·3	101·3	−1·0
48.	*p*-Iodotoluene	C_7H_7I	S.	109·6	107·5	−1·9
49.	*n*-Octyl chloride	$C_8H_{17}Cl$	P.	140·4	142·0	+1·2
50.	*n*-Octyl bromide	$C_8H_{17}Br$	„	144·7	144·8	+0·1
51.	*n*-Octyl iodide	$C_8H_{17}I$	„	150·4	151·0	+0·4

TABLE VI.

Ethers.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
52.	Ethylene oxide	C_2H_4O	M. & B.	37·7	38·8	+2·9
53.	Epichlorohydrin	C_3H_5OCl	J.	63·6	65·9	+3·6
	„	„	S. & W.	65·5	„	+0·7
54.	Ethyl ether	$C_4H_{10}O$	Y.	77·1	76·4	−0·9
55.	Paraldehyde	$C_6H_{12}O_3$	P.	(106·4)	102·6	−3·6
56.	Acetal	$C_6H_{14}O_2$	W.	112·2	110·4	−1·7
57.	Anisole	C_7H_8O	P., Sch.	90·8	90·9	+0·1
58.	Phenetole	$C_8H_{10}O$	„	105·5	105·4	−0·1
	„	„	B.	104·2	„	+1·2
59.	*m*-Tolyl methyl ether	„	P.	(103·9)	„	+1·5
60.	*p*- „ „ „	„	„	(104·0)	„	+1·4
61.	Veratrole	$C_8H_{10}O_2$	J.	106·1	110·4	+4·1
62.	Dimethylresorcinol	„	P.	109·2	„	+1·1
63.	Phenyl propyl ether	$C_9H_{12}O$	„	(117·9)	119·9	+1·7
64.	Phenyl *iso*propyl ether	„	„	(117·5)	„	+2·0
65.	Phenyl octyl ether	$C_{14}H_{22}O$	„	(188·7)	192·4	+1·9

deviations occur in compounds containing several halogen atoms, *e.g.*, ethylene dichloride (No. 35) and acetylene tetrachloride (No. 33). Since, however, carbon tetrachloride gives a satisfactory agreement, it is probable that these discrepancies are due to errors of observation. The long series of esters in Table VIII gives a test of accuracy of the additive properties of V_0 over a large range of molecular weight, and affords, in general, excellent support for the views now advanced.

TABLE VII.

Aldehydes and Ketones.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
66. Acetone	C_3H_6O	B.	56·0	56·5	+0·9
67. Methyl ethyl ketone	C_4H_8O	T. & J.	71·8	71·0	−1·1
68. Furfural	$C_5H_4O_2$	W.	68·5	68·1	−0·6
,,	,,	J.	68·7	,,	−0·9
69. Acetylacetone	$C_5H_8O_2$	,,	84·5	85·1	+0·7
70. Methyl propyl ketone	$C_5H_{10}O$	T. & J.	85·2	85·5	+0·4
71. Diethyl ketone	,,	,,	84·3	,,	+1·4
72. Ethyl acetoacetate	$C_6H_{10}O_3$	P.	103·8	104·6	+0·8
73. Benzaldehyde	C_7H_6O	,,	85·3	85·5	+0·3
74. Dimethylacetylacetone	$C_7H_{12}O_2$	,,	111·6	114·1	+2·3
75. Dipropyl ketone	$C_7H_{14}O$	,,	113·9	114·5	+0·5
76. Acetophenone	C_8H_8O	,,	97·8	100·0	+2·2
77. Benzylideneacetone	$C_{10}H_{10}O$	,,	123·8	123·6	−0·2
78. Benzophenone	$C_{13}H_{10}O$	,,	141·3	143·5	+1·6

TABLE VIII.

Esters.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
79. Methyl formate	$C_2H_4O_2$	Y.	46·7	47·0	+0·7
80. Methyl acetate	$C_3H_6O_2$	,,	61·1	61·5	+0·7
81. Ethyl formate	,,	,,	61·9	,,	−0·7
82. Methyl propionate	$C_4H_8O_2$	,,	75·5	76·0	+0·7
83. Ethyl acetate	,,	,,	76·4	,,	−0·5
,, ,,	,,	W.	75·9	,,	+0·1
84. *n*-Propyl formate	,,	Y.	76·7	,,	−0·9
85. Methyl *n*-butyrate	$C_5H_{10}O_2$	,,	90·7	90·5	−0·2
86. Methyl *iso*butyrate	,,	,,	90·6	,,	−0·1
87. Ethyl propionate	,,	,,	90·9	,,	−0·4
88. Propyl acetate	,,	,,	91·3	,,	−0·9
89. Ethyl carbonate	$C_5H_{10}O_3$	S. R. & W.	98·2	95·5	−2·7
90. Methyl maleate	$C_6H_6O_4$	S. & Wh.	103·8	104·2	+0·4
91. Methyl fumarate	,,	,,	107·5	,,	−3·2
92. *d*-β-Butyl acetate	$C_6H_{12}O_2$	P. & K.	106·1	105·0	−1·1
93. Methyl citraconate	$C_7H_{10}O_4$	S. & Wh.	117·1	118·7	+1·4
94. Methyl mesaconate	,,	,,	116·0	,,	+2·3
95. Ethyl *cyclo*butanecarboxylate	$C_7H_{12}O_2$	S. & W.	108·5	109·3	+0·7
96. *d*-β-Butyl propionate	$C_7H_{14}O_2$	P. & K.	121·5	119·5	−1·7
97. Methyl benzoate	$C_8H_8O_2$	P.	(104·3)	105·0	+0·7
98. Phenyl acetate	,,	,,	104·8	,,	+0·2
99. *d*-β-Butyl *n*-butyrate	$C_8H_{16}O_2$	P. & K.	134·4	134·0	−0·3
100. *d*-β-Hexyl acetate	,,	,,	135·5	,,	−1·1

TABLE VIII (*contd.*)

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 calc.).	Diff., %.
101.	Ethyl 1-cyano*cyclo*butane-1-carboxylate...	$C_8H_{11}O_2N$	S. & W.	122·5	122·8	+0·3
102.	Ethyl benzoate	$C_9H_{10}O_2$	P.	(119·0)	119·5	+0·4
103.	Ethyl *cyclo*propane-1 : 1-dicarboxylate ...	$C_8H_{14}O_4$	S. & W.	145·4	144·5	−0·6
104.	Ethyl *cyclo*propane-1 : 2-dicarboxylate ...	,,	,,	146·0	,,	−1·0
105.	Ethyl *n*-heptoate	$C_9H_{18}O_2$	P.	149·6	148·5	−0·7
106.	*d*-β-Butyl *n*-valerate	,,	P. & K.	150·8	,,	−1·5
107.	*d*-β-Hexyl propionate ...	,,	,,	149·7	,,	−0·8
108.	*d*-β-Heptyl acetate	,,	,,	150·5	,,	−1·3
109.	Methyl cinnamate	$C_{10}H_{10}O_2$	S. & Wh.	127·5	128·6	+0·9
110.	Methyl *allo*cinnamate ...	,,	,,	124·3	,,	+3·6
111.	*n*-Propyl benzoate	$C_{10}H_{12}O_2$	P.	(133·5)	134·0	+0·4
112.	*iso*Propyl benzoate	,,	,,	(136·6)	,,	−1·9
113.	Ethyl *o*-toluate	,,	,,	(131·7)	,,	+1·7
114.	Ethyl *p*-toluate	,,	,,	(133·3)	,,	+0·6
115.	Ethyl phenylacetate	,,	,,	(130·2)	,,	+2·8
116.	Ethyl *o*-methoxybenzoate	$C_{10}H_{12}O_3$	,,	(135·1)	139·0	+2·9
117.	Ethyl *m*-methoxybenzoate	,,	,,	(137·1)	,,	+1·4
118.	Ethyl anisate	,,	,,	(136·7)	,,	+1·7
119.	Ethyl *cyclo*butane-1 : 1-dicarboxylate	$C_{10}H_{16}O_4$	S. & W.	158·4	157·4	−0·7
120.	*d*-β-Butyl *n*-hexoate	$C_{10}H_{20}O_2$	P. & K.	164·8	163·0	−1·2
121.	*d*-β-Hexyl *n*-butyrate ...	,,	,,	161·2	,,	+1·2
122.	*d*-β-Heptyl propionate ...	,,	,,	164·7	,,	+1·1
123.	*d*-β-Octyl acetate	,,	,,	164·6	,,	+1·0
124.	Methyl α-bromocinnamate	$C_{10}H_9O_2Br$	S. & Wh.	138·7	136·0	−2·0
125.	Methyl α-bromo*allo*cinnamate	,,	,,	140·4	,,	−3·2
126.	Methyl β-bromocinnamate	,,	,,	139·5	,,	−2·5
127.	Methyl β-bromo*allo*cinnamate	,,	,,	142·4	,,	−4·7
128.	Ethyl cinnamate	$C_{11}H_{12}O_2$	P.	141·9	143·1	+0·8
129.	Ethyl benzoylacetate ...	$C_{11}H_{12}O_3$	,,	145·6	148·1	+1·7
130.	Ethyl phenylpropionate	$C_{11}H_{14}O_2$	,,	146·7	148·5	+1·2
131.	*n*-Butyl benzoate	,,	,,	(147·4)	,,	+0·7
132.	*iso*Butyl benzoate	,,	,,	(148·5)	,,	±0·0
133.	Ethyl *p-iso*propylbenzoate	,,	,,	(149·5)	,,	−0·7
134.	Ethyl caronate	$C_{11}H_{18}O_4$	S. & W.	171·4	173·5	+1·2
135.	*d*-β-Butyl *n*-heptoate ...	$C_{11}H_{22}O_2$	P. & K.	179·6	177·5	−1·2
136.	*d*-β-Hexyl *n*-valerate ...	,,	,,	179·0	,,	−0·9
137.	*d*-β-Heptyl *n*-butyrate ...	,,	,,	179·7	,,	−1·2
138.	*d*-β-Octyl propionate ...	,,	,,	177·6	,,	−0·1
139.	Ethyl phthalate.....	$C_{12}H_{14}O_4$	P.	168·0	167·6	−0·3
140.	Ethyl terephthalate	,,	,,	168·2	,,	−0·4
141.	*d*-β-Butyl *n*-octoate	$C_{12}H_{24}O_2$	P. & K.	195·5	192·0	−1·8
142.	*d*-β-Hexyl *n*-hexoate	,,	,,	194·0	,,	−1·0
143.	*d*-β-Heptyl *n*-valerate ...	,,	,,	194·1	,,	−1·1
144.	*d*-β-Octyl *n*-butyrate ...	,,	,,	194·2	,,	−1·1
145.	Phenyl carbonate	$C_{13}H_{10}O_3$	S. R. & W.	157·2	153·5	−2·4
146.	Ethyl α-naphthoate	$C_{13}H_{12}O_2$	P.	151·9	153·9	+1·3
147.	Ethyl β-naphthoate	,,	,,	152·7	,,	+0·8
148.	Phenyl *n*-heptoate	$C_{13}H_{18}O_2$	,,	175·5	177·5	+1·2
149.	*d*-β-Butyl *n*-nonoate	$C_{13}H_{26}O_2$	P. & K.	207·3	206·5	−0·4
150.	*d*-β-Hexyl *n*-heptoate ...	,,	,,	207·6	,,	−0·5

TABLE VIII (*contd.*)

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
151. *d*-β-Heptyl *n*-hexoate ...	$C_{13}H_{26}O_2$	P. & K.	210·2	206·5	−1·8
152. *d*-β-Octyl *n*-valerate	,,	,,	209·5	,,	−1·5
153. *d*-β-Undecyl acetate	,,	,,	207·6	,,	−0·5
154. *d*-β-Heptyl *n*-heptoate ...	$C_{14}H_{28}O_2$	,,	223·2	221·0	−1·0
155. *d*-β-Octyl *n*-hexoate	,,	,,	223·3	,,	−1·1
156. *d*-β-Undecyl propionate...	,,	,,	222·6	,,	−0·7
157. *n*-Octyl benzoate	$C_{15}H_{22}O_2$	P.	(203·4)	206·5	+1·6
158. Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate	$C_{15}H_{22}O_8$	S. & W.	242·0	240·7	−0·5
159. *d*-β-Butyl *n*-undecoate ...	$C_{15}H_{30}O_2$	P. & K.	237·2	235·5	−0·7
160. *d*-β-Hexyl *n*-nonoate	,,	,,	236·3	,,	−0·4
161. *d*-β-Heptyl *n*-octoate ...	,,	,,	238·1	,,	−1·1
162. *d*-β-Octyl *n*-heptoate ...	,,	,,	237·0	,,	−0·7
163. *d*-β-Undecyl *n*-butyrate...	,,	,,	236·5	,,	−0·4
164. *d*-β-Butyl *n*-dodecoate ...	$C_{16}H_{32}O_2$	,,	252·1	250·0	−0·8
165. *d*-β-Heptyl *n*-nonoate ...	,,	,,	252·2	,,	−0·9
166. *d*-β-Octyl *n*-octoate	,,	,,	251·5	,,	−0·6
167. *d*-β-Undecyl *n*-valerate ...	,,	,,	250·8	,,	−0·3
168. *d*-β-Hexyl *n*-undecoate ...	$C_{17}H_{34}O_2$	,,	264·5	264·5	±0·0
169. *d*-β-Octyl *n*-nonoate	,,	,,	266·8	,,	−0·9
170. *d*-β-Undecyl *n*-hexoate ...	,,	,,	265·2	,,	−0·3
171. *d*-β-Butyl myristate	$C_{18}H_{36}O_2$	,,	280·2	279·0	−0·4
172. *d*-β-Hexyl *n*-dodecoate ...	,,	,,	278·7	,,	+0·1
173. *d*-β-Heptyl *n*-undecoate	,,	,,	280·0	,,	−0·4
174. *d*-β-Undecyl *n*-heptoate...	,,	,,	279·7	,,	−0·3
175. *d*-β-Heptyl *n*-dodecoate...	$C_{19}H_{38}O_2$	,,	296·6	293·5	−1·0
176. *d*-β-Octyl *n*-undecoate ...	,,	,,	294·2	,,	−0·2
177. *d*-β-Butyl palmitate	$C_{20}H_{40}O_2$	,,	307·1	308·0	+0·3
178. *d*-β-Hexyl myristate	,,	,,	307·3	,,	+0·2
179. *d*-β-Octyl *n*-dodecoate ...	,,	,,	308·3	,,	−0·1
180. *d*-β-Undecyl *n*-nonoate ...	,,	,,	307·7	,,	+0·1
181. *d*-β-Heptyl myristate.....	$C_{21}H_{42}O_2$	,,	323·1	322·5	−0·2
182. *d*-β-Butyl stearate	$C_{22}H_{44}O_2$	,,	334·7	337·0	+0·7
183. *d*-β-Hexyl palmitate	,,	,,	337·0	,,	±0·0
184. *d*-β-Octyl myristate	,,	,,	337·6	,,	−0·2
185. *d*-β-Undecyl *n*-undecoate	,,	,,	335·1	,,	+0·6
186. *d*-β-Heptyl palmitate.....	$C_{23}H_{46}O_2$	,,	352·3	351·5	−0·2
187. *d*-β-Undecyl *n*-dodecoate	,,	,,	349·9	,,	+0·5
188. *d*-β-Hexyl stearate	$C_{24}H_{48}O_2$	,,	360·6	366·0	+1·5
189. *d*-β-Octyl palmitate	,,	,,	376·1	,,	−2·8
190. *d*-β-Heptyl stearate	$C_{25}H_{50}O_2$	,,	377·2	380·5	+0·9
191. *d*-β-Undecyl myristate ...	,,	,,	377·2	,,	+0·9
192. *d*-β-Octyl stearate	$C_{26}H_{52}O_2$	,,	403·9	395·0	−2·2

Table IX contains the data for a number of nitro-compounds for which the structure $-N\begin{matrix}O\\ \diagup\\ \diagdown\\ O\end{matrix}$, containing one non-polar and one semipolar bond, has been assumed. If both the double bonds were non-polar, the value of V_0 (calc.) would have to be increased by 8·0 c.c. and would be much larger than the experimental figures.

The nitriles in Table X are assumed to have the structure $-C\equiv N$, which is confirmed by the good agreement between the observed and the calculated values. The same conclusion has been reached from

study of the parachor of a number of nitriles (Sugden and Wilkins, *loc. cit.*), so that Langmuir's assumption of a special structure containing two kernels within one octet is unnecessary.

TABLE IX.

Nitro-compounds.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
193.	Nitromethane	CH_3O_2N	W.	42·6	42·8	+0·5
	,,	,,	J.	42·9	,,	−0·2
194.	Ethyl nitrate	$C_2H_5O_3N$	W.	64·6	62·3	+3·5
195.	Nitrobenzene	$C_6H_5O_2N$	Y.	88·0	86·3	−1·9
	,,	,,	W.	86·0	,,	+0·4
196.	*m*-Fluoronitrobenzene	$C_6H_4O_2NF$	J.	89·7	89·9	+0·2
197.	*p*-Fluoronitrobenzene	,,	,,	89·0	,,	+1·0
198.	*o*-Chloronitrobenzene	$C_6H_4O_2NCl$	S. & W.	97·8	98·9	+1·1
199.	*m*- ,,	,,	,,	97·9	,,	+1·0
200.	*p*- ,,	,,	J.	102·1	,,	−3·2
201.	*o*-Bromonitrobenzene	$C_6H_4O_2NBr$	S. & W.	100·9	101·7	+0·8
202.	*m*- ,,	,,	,,	102·0	,,	−0·3
203.	*p*- ,,	,,	,,	103·3	,,	−1·6
204.	*o*-Nitrotoluene	$C_7H_7O_2N$	,,	99·3	100·8	+1·5
205.	*m*- ,,	,,	,,	100·0	,,	+0·8
206.	*p*- ,,	,,	,,	102·2	,,	−1·4

TABLE X.

Nitriles.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
207.	Acetonitrile	C_2H_3N	W.	40·6	41·4	+1·9
208.	Malononitrile	$C_3H_2N_2$	W. & S.	52·3	54·9	+5·0
209.	Propionitrile	C_3H_5N	W.	55·3	55·9	+1·2
210.	Methyl cyanoacetate	$C_4H_5O_2N$	J.	74·4	75·0	+0·8
211.	Ethyl cyanoacetate	$C_5H_7O_2N$	,,	88·2	89·5	+1·5
	,, ,,	,,	W. & S.	87·8	,,	+1·9
212.	Benzonitrile	C_7H_5N	W.	85·6	84·9	−0·8
213.	Phenylacetonitrile	C_8H_7N	,,	97·1	99·4	+2·3
214.	*o*-Toluonitrile	,,	S. & W.	100·6	,,	−1·2
215.	*m*- ,,	,,	,,	100·3	,,	−0·9
216.	*p*- ,,	,,	,,	101·1	,,	−1·7

TABLE XI.

Phosphorus Compounds.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
217.	Phosphorus trichloride	PCl_3	Th.	69·6	70·6	+1·4
218.	Phosphorus tribromide	PBr_3	S. R. & W.	78·6	79·0	+0·5
219.	Phosphorus oxychloride	$POCl_3$	,,	73·4	75·6	+3·0
220.	Triethyl phosphate	$C_6H_{15}O_4P$	,,	140·5	139·8	−0·5
221.	Triphenylphosphine	$C_{18}H_{15}P$	W. & S.	206·4	206·8	+0·2
222.	Triphenyl phosphate	$C_{18}H_{15}O_4P$	S. R. & W.	(230·2)	226·8	−1·5

Tables XI and XII record data for a number of compounds of phosphorus and sulphur. A good agreement between V_0 (obs.) and V_0 (calc.) is found in most cases, both in compounds containing only non-polar linkages and in those containing semipolar double bonds.

TABLE XII.

Sulphur Compounds.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
223.	Thionyl chloride	$SOCl_2$	S. R. & W.	58·0	57·9	−0·2
224.	Sulphuryl chloride	SO_2Cl_2	,,	62·6	62·9	+0·5
225.	Sulphur monochloride	S_2Cl_2	J.	67·1	67·2	+0·1
226.	Carbon disulphide	CS_2	,,	48·2	45·7	+5·1
227.	Methyl thiocyanate	C_2H_3NS	W.	54·9	55·7	+1·5
228.	Methyl sulphate	$C_2H_6O_4S$	S. R. & W.	78·5	76·7	−2·3
229.	Thiophen	C_4H_4S	J.	63·5	63·3	−0·3
230.	Ethyl sulphite	$C_4H_{10}O_3S$	W. & S.	101·1	100·7	−0·4
231.	Ethyl ethanesulphonate	,,	,,	96·7	,,	+4·0
232.	Ethyl sulphate	$C_4H_{10}O_4S$	S. R. & W.	107·3	105·7	−1·5
233.	Thiophenol	C_6H_6S	W. & S.	85·6	85·7	+0·1
234.	Diphenyl sulphide	$C_{12}H_{10}S$	P.	143·0	143·7	+0·5
235.	Dibenzyl sulphide	$C_{14}H_{14}S$	,,	170·8	172·7	+1·1

(4) *Associated Liquids.*

It has been shown (preceding paper) that acetic acid and ethyl alcohol deviate from the requirements of equation (1) at high temperatures, but that at lower temperatures they give a satisfactory agreement. For acetic acid, in fact, the deviation only becomes appreciable in the neighbourhood of the critical temperature; it is therefore to be expected that the value of V_0 calculated from density observations at lower temperatures will be reproduced by adding together suitable constants from Table II. The data in Table XIII show that this is substantially true for a number of acids.

TABLE XIII.

Acids.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
236.	Formic acid	CH_2O_2	W.	30·7	32·5	+5·8
237.	Acetic acid	$C_2H_4O_2$	Y.	46·7	47·0	+0·7
238.	Monochloroacetic acid	$C_2H_3O_2Cl$	J.	56·4	59·6	+5·7
239.	Dichloroacetic acid	$C_2H_2O_2Cl_2$	,,	69·1	72·2	+4·4
240.	Trichloroacetic acid	$C_2HO_2Cl_3$	,,	83·3	84·8	+1·8
241.	Propionic acid	$C_3H_6O_2$	P.	60·8	61·5	+1·2
242.	*n*-Heptoic acid	$C_7H_{14}O_2$	,,	118·3	119·5	+1·1
243.	Nitric acid	HNO_3	V. & M.	32·7	33·3	+1·9
244.	Sulphuric acid	H_2SO_4	W.	47·1	47·7	+1·3
245.	Perchloric acid	$HClO_4$	Wi.	45·7	46·0	+0·6

For the alcohols, association appears to produce a small contraction in volume, and with the exception of methyl and ethyl alcohols the observed values are satisfactorily reproduced (Table XIV) by giving oxygen the value 3·0 in alcohols instead of the usual value O = 5·0. A somewhat larger contraction is found for amines (Table XV), for which N = 0 is used instead of 3·6 as in other nitrogen compounds. This contraction in zero volume is probably not a real change in volume but may be accounted for as follows. It seems probable from the behaviour of acetic acid and ethyl alcohol that equation (1) holds so long as the degree of association remains unchanged with increasing temperature, but that if the degree of association alters then the density decreases with temperature more rapidly than is predicted by this equation. For observations below the boiling point, the effect is small, and produces a small increase in the rate of change of density with temperature, which on extrapolation gives rather too high a value for the zero density, and consequently too small a value for the zero volume. This explanation is supported by the fact that methyl and ethyl alcohols, for which equation (1) holds up to temperatures well above the boiling points, do not exhibit this contraction, but give values for oxygen of about 5·0.

TABLE XIV.

Alcohols.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
246.	Methyl alcohol	CH_4O	Y.	32·3	30·9	−4·3
247.	Ethyl alcohol	C_2H_6O	,,	46·8	45·4	−2·9
248.	Ethylene glycol	$C_2H_6O_2$	W.	48·4	48·4	±0·0
249.	*n*-Propyl alcohol	C_3H_8O	P.	60·6	59·9	−1·2
250.	*d*-Methylethylcarbinol	$C_4H_{10}O$	P. & K.	74·4	74·4	±0·0
251.	*d*-Methyl-*n*-propylcarbinol	$C_5H_{12}O$	,,	88·1	88·9	+0·9
252.	Phenol	C_6H_6O	P.	74·3	74·4	+0·1
	,,	,,	B.	74·3	,,	+0·1
253.	*d*-Methyl-*n*-butylcarbinol	$C_6H_{14}O$	P. & K.	102·4	103·4	+1·0
254.	*o*-Chlorophenol	C_6H_5OCl	B.	86·2	87·0	+0·9
255.	*o*-Cresol	C_7H_8O	,,	86·9	88·9	+2·3
256.	*m*- ,,	,,	,,	88·6	,,	+0·4
257.	*p*- ,,	,,	,,	89·5	,,	−0·7
258.	Benzyl alcohol	,,	P.	88·3	,,	+0·7
	,, ,,	,,	W.	87·9	,,	+1·1
259.	*d*-Methyl-*n*-amylcarbinol	$C_7H_{16}O$	P. & K.	116·2	117·9	+1·5
260.	Methyl salicylate	$C_8H_8O_3$	P.	106·6	108·0	+1·3
261.	Cinnamyl alcohol	$C_9H_{10}O$	,,	110·2	112·5	+2·1
262.	Ethyl salicylate	$C_9H_{10}O_3$	,,	122·3	122·5	+0·2
263.	*d*-Methyl-*n*-heptylcarbinol	$C_9H_{20}O$	P. & K.	145·3	146·9	+1·1
264.	Cuminol	$C_{10}H_{14}O$	P.	135·1	132·4	−2·0
265.	Thymol	,,	,,	130·4	,,	+1·8
266.	*d*-Methyl-*n*-octylcarbinol	$C_{10}H_{22}O$	P. & K.	159·7	161·4	+1·1
267.	*d*-Methyl-*n*-nonylcarbinol	$C_{11}H_{24}O$	,,	174·3	175·9	+0·9
268.	*d*-Methyl-*n*-decylcarbinol	$C_{12}H_{26}O$	,,	186·4	190·4	+2·3

TABLE XV.

Amines.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
269.	Ammonia	NH_3		19·1	20·1	+5·0
270.	Methylamine	CH_5N	J.	33·7	34·6	+2·7
271.	Dimethylamine	C_2H_7N	,,	50·1	49·1	−2·0
272.	Ethylamine	,,	,,	48·2	,,	+1·8
273.	Trimethylamine	C_3H_9N	,,	65·6	63·6	−3·0
274.	*n*-Propylamine	,,	,,	62·7	,,	+1·4
275.	Diethylamine	$C_4H_{11}N$	,,	78·0	78·1	+0·1
276.	Piperidine	$C_5H_{11}N$	,,	79·7	79·8	+0·1
277.	Aniline	C_6H_7N	Y.	77·7	78·1	+0·4
	,,	,,	B.	76·8	,,	+1·7
278.	*m*-Phenylenediamine	$C_6H_8N_2$	P.	82·5	84·8	+2·8
279.	Triethylamine	$C_6H_{15}N$	J.	108·1	107·1	−0·9
280.	Di-*n*-propylamine	,,	,,	108·0	,,	−0·8
281.	*o*-Toluidine	C_7H_9N	P.	90·5	92·6	+2·3
282.	Benzylamine	,,	,,	91·2	,,	+1·5
283.	Dimethylaniline	$C_8H_{11}N$	,,	105·7	107·1	+1·3
284.	Tripropylamine	$C_9H_{21}N$	J.	153·1	150·6	−1·7

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Summary.

(1) It has been shown that zero volumes can be predicted by adding together certain characteristic constants for the atoms and structures present in the molecule. Of the 284 compounds considered, 236 are within 2% and 149 within 1% of the calculated value. The agreement is not quite so good as is found with the parachor; the zero volume is, however, extrapolated from the

experimental data and is therefore subject to a greater error in its determination.

(2) Non-polar and semi-polar double bonds can be clearly distinguished by their effect upon the zero volume.

(3) The zero volumes of associated liquids, *e.g.*, alcohols and amines, can be predicted by making a small change in the values for oxygen and nitrogen.

BIRKBECK COLLEGE,
UNIVERSITY OF LONDON, E.C. 4. [*Received, June 10th*, 1927.]

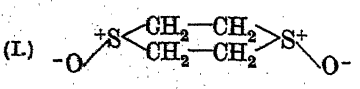
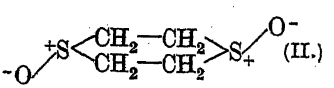
CCXXXV.—cis-trans-*Isomerism of Disulphoxides.*

By ERNEST VERE BELL and GEORGE MACDONALD BENNETT.

THE isolation of optically active ethyl *p*-toluenesulphinate (Phillips, J., 1925, **127**, 2552) and optically active sulphoxides of the type RR'SO (Harrison, Kenyon, and Phillips, J., 1926, 2079) proves that the three groups attached to the sulphur atom in these compounds do not lie in one plane with it. It follows that, if two sulphoxyl groups are present in a molecule, two isomerides should arise having the *cis*- and the *trans*-configuration, respectively. No such isomerism has hitherto been observed, although suitable disulphoxides have been known for half a century. We have therefore subjected two such cases to a closer investigation and have in each case isolated a pair of isomeric disulphoxides.

The so-called disulphoxides derived from the disulphides R·S·S·R′ are not in question, for it has become clear that they do not actually possess the disulphoxide structure R·SO·SO·R′, but are of the type R·S·SO_2·R′ (Smiles and Gibson, J., 1924, **125**, 176; Miller and Smiles, J., 1925, **127**, 224).

The simplest case is presented by the disulphoxides (I) and (II) of diethylene disulphide (1 : 4-dithian).

(I.)   (II.)

Here the plane of symmetry present in the molecule of each isomeride excludes the possibility of enantiomorphism. A disulphoxide of 1 : 4-dithian was isolated by Crafts (*Annalen*, 1862, **124**, 110; 1863, **125**, 123), which was soluble in water and separated from it in rhomb-shaped crystals. An examination of the mother-liquor from the crystallisation of this substance has now revealed the presence of an isomeride. The two disulphoxides decompose without melting, and their characterisation has depended on their

differences in solubility and in crystallographic properties. The α-isomeride is monoclinic and its solubility in 90% ethyl alcohol is less than one-fifth of that of the β-form, which is anorthic. The alternative formula $S<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>SO_2$, which might represent one of the isomerides as structurally isomeric, is inadmissible, for both the α- and the β-isomeride are readily reduced to the parent disulphide, a reaction characteristic of sulphoxides, but never shown by sulphones.

The configurations of these disulphoxides cannot be determined with certainty, but it may be tentatively assumed that the α-isomeride, being the less soluble, is the *trans*-form (II). Attempts to convert one isomeride into the other by heating in aqueous solution alone, or with acetic or hydrochloric acid of various concentrations, were unsuccessful. When heated with 5—20% hydrochloric acid, both disulphoxides behaved as peroxides, yielding dithian itself. The fact that it was not possible to bring about the interconversion of these isomeric disulphoxides is surprising, yet it is in agreement with the stability of the optically active sulphoxides, which showed no marked tendency to racemisation.

There is reason to suppose that the dissolution of an aldehyde or ketone in water involves the formation of a compound of the type $R{\cdot}C(OH)_2{\cdot}R'$, and with the older formulation of sulphoxides their ready solubility in water would by analogy have been attributed to the formation of a corresponding compound $R{\cdot}S(OH)_2{\cdot}R'$. If this were so, it would involve the rapid racemisation of active sulphoxides and the easy interconversion of *cis-trans*-isomerides in aqueous solution. On the other hand, from a consideration of the electronic formulæ it is clear that a compound $R{\cdot}S(OH)_2{\cdot}R'$ cannot exist as such, but only as the two ions: $R:\underset{\underset{H}{\vdots O:}}{\overset{\cdot\cdot}{S}}:R'$ and $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$. Yet solutions of sulphoxides are not markedly alkaline, so that a complex, if it exists, must occur largely in some non-dissociated form. These considerations point to the following formula as a probable one: $\begin{matrix}R\\R'\end{matrix}\!\!>\!S:O:H:O:H$ (compare formulæ suggested for weak nitrogen bases by Moore and Winmill, J., 1912, **101**, 1635; Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1419).

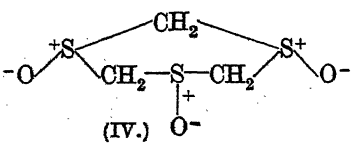
The disulphoxide derived from diethyldithiolethane,

$$CH_2(SEt){\cdot}CH_2{\cdot}SEt,$$

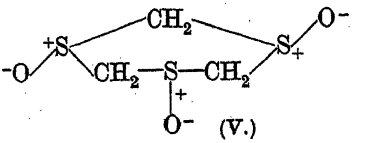
was described by Beckmann in 1878 (*J. pr. Chem.*, 1878, **17**, 409). We have examined the oxidation of the closely related dimeth[illegible]

dithiolethane. The product of the reaction is a mixture of two isomeric disulphoxides, $Me{\cdot}SO{\cdot}C_2H_4{\cdot}SOMe$, the α-form, m. p. 163—164°, being less soluble in various solvents than the β-form, m. p. 128—130°. Both are readily reduced to the disulphide. One of these isomerides must be an inactive mixture (or compound) of two enantiomorphs, but it is not possible to discriminate between them. This pair of isomerides is closely analogous to the two diethiodides of the same disulphide which were recently described by Wedekind (*Ber.*, 1925, **58**, 2510).

It follows from the results now described that a cyclic trisulphoxide also should occur in two forms, and it is possible that the two isomeric trisulphoxides of trimethylene trisulphide obtained by Hinsberg (*J. pr. Chem.*, 1912, **85**, 1912; 1914, **89**, 547) are, in fact, the two substances (IV) and (V).



(IV.)



(V.)

The criticisms of Fromm and Schultis (*Ber.*, 1923, **56**, 937), however, suggest the advisability of a reinvestigation of this case.

We are indebted to Professor S. Smiles, F.R.S., for drawing our attention to the isomeric disulphoxides of thianthren (Fries and Vogt, *Ber.*, 1911, **44**, 756). The isomerism in this case is well established, but it has hitherto remained unexplained. It is evidently another example of the phenomenon under discussion.

Experimental.

Oxidation of 1 : 4-*Dithian by Hydrogen Peroxide.*—To a solution of dithian (10 g.) in glacial acetic acid (200 c.c.) at 0°, hydrogen peroxide (2 mols. of 30% aqueous solution), dissolved in an equal volume of acetic acid, was added, and the mixture kept for 24 hours. Most of the acetic acid and any trace of unchanged sulphide were then removed in a current of steam and the solution was evaporated to dryness three times to remove acetic acid (yield, 12·5 g. of crude disulphoxides). The product consisted mainly of the α-disulphoxide, which is undoubtedly that described by Crafts. Crystallisation of the crude mixture from 90% ethyl alcohol (400 c.c.) yielded this compound, and one further crystallisation from 50% ethyl alcohol (50 c.c.) gave the pure substance (7·8 g.) in rhomb- or hexagonal-shaped plates, decomp. 263° (uncorr.) (Found: C, 31·3; H, 5·4; *M*, cryoscopic in water, 142, 149. Calc.: C, 31·55; H, 5·3%; *M*, 152).

The substance is readily soluble in cold water and practically insoluble in absolute ethyl alcohol and other organic solvents. It crystallises in the monoclinic system, having $a:b:c = 1{\cdot}267:1:0{\cdot}979$; $\beta = 104°\ 3'$. Crystals of the habit shown in Fig. 1 were obtained by slow evaporation of an aqueous solution. The following is a list of the forms and the angular measurements observed with three crystals:

	a (100).	*m* (110).	*r* (101).	*R* (1̄01).	*q* (011).
ϕ	0° 0′	*50° 52′	0° 0′	180° 0′	*75° 40′
ρ	90° 0′	90° 0′	46° 18′	28° 32′	*45° 19′

The simpler rhomb-shaped crystals are developed on *R* bounded by *q* and *m*. The angle of the rhomb was observed under the microscope to be about 71° (calc., 71° 6′). The extinction on the face *R* is oblique. The position of the optic axes was not observed. The crystals had $d_4^{20°}$ (vac.) 1·570.

By fractional crystallisation of the material retained in the mother-liquor of this sulphoxide a small amount of another, more soluble substance was obtained, which crystallised in needles from absolute ethyl alcohol. The separation was facilitated by the fact that the two substances, although not very different in microscopic appearance in ordinary light, were sharply differentiated when seen between crossed Nicols. The second isomeride was best obtained thus: The crude mixture of disulphoxides (6·2 g.) was warmed with aqueous alcohol (90%, 200 c.c.), and then cooled in ice, and the solution was filtered. The solid residue (4·3 g.) was almost pure α-disulphoxide. The solution on evaporation left a residue (1·9 g.), which was boiled with enough absolute ethyl alcohol to dissolve about half of it. The solution was filtered and, on cooling, it deposited the β-*isomeride* (0·8 g.), which was pure after one further crystallisation (Found: C, 31·55; H, 5·2; *M*, 132, 144. $C_4H_8O_2S_2$ requires C, 31·55; H, 5·3%; *M*, 152).

β-*Dithian dioxide* separates from aqueous or absolute alcohol in elongated plates or flat needles, decomp. 235—250°. It crystallises in the anorthic system, having the angular elements *ab*, 105° 0′; *d*, 56° 17′; *e*, 127° 14′; *f*, 61° 44′; and *g*, 120° 59′. Crystals of the habit shown in Fig. 2 were obtained by slow crystallisation of an aqueous solution. The following forms and mean angular values were observed with three crystals:

	a (100).	*b* (010).	*c* (001).	*o* (111).
ϕ	0° 0′	*105° 0′	*241° 11′	*60° 28′
ρ	90° 0′	90° 0′	*40° 56′	*37° 29′

The extinction on *a* is at about 4° to the edge *ab*. The biaxial optic picture is seen in convergent light on face *a*, the optic axial

plane being nearly parallel to the edge *ab* and the acute bisectrix nearly normal to *a*. $d_4^{20°}$ (vac.) 1·554.

Determinations of Solubility and Proportion of the Isomerides present.—100 C.c. of ethyl alcohol dissolve less than 1 g. of the α-isomeride at the boiling point, and approximately 0·1 g. at 20°; the β-isomeride is three times as soluble in cold alcohol. The solubilities of the two substances in 90·7% ethyl alcohol were determined accurately in a thermostat at 22·0°. 100 C.c. of solution contained 0·38 g. of α-isomeride and 2·26 g. of β-isomeride. Use being made of these values, the proportion of the two isomerides present in the oxidation product was determined. The mixture (0·4006 g. made by means of hydrogen peroxide) was stirred for several hours in a closed bottle at 22·0° with 90·7% alcohol (25·0 c.c.); 10 c.c. of the solution then contained 0·0557 g. of material (mean

FIG. 1.

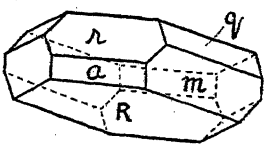
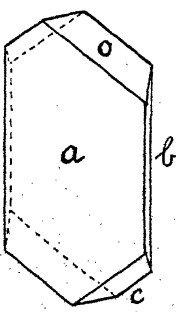


FIG. 2.



value). The influence of each on the solubility of the other being neglected, the two must be present in the proportion of 11·0% of the β- and 89·0% of the α-isomeride. A similar determination on the product of oxidation of dithian in ether by means of nitrous fumes showed the presence of 8·9% of the β-isomeride.

Reduction of the Disulphoxides.—A solution of the α-disulphoxide in acetic acid was boiled with addition of hydrochloric acid and zinc dust in excess. The solution when diluted and cooled deposited crystals of dithian (yield more than 50% of the theoretical), which was identified by direct comparison and the m. p. of a mixture with pure dithian. When the β-disulphoxide was reduced in the same way, dithian was again produced in quantity.

Attempted Interconversion of the Isomerides.—The α-disulphoxide was boiled for several hours in aqueous solution, and a known amount of ethyl alcohol then added. The weight of α-isomeride so recovered was exactly that expected, and therefore no conversion of α- into β-isomeride had occurred. The experiment was repeated with addition of acetic and dilute hydrochloric acids, but no positive

evidence of interconversion was obtained. When either isomeride was heated under reflux or in a sealed tube with hydrochloric acid (5—35%), dithian was always produced; it was identified as before. The second isomeride was in no case detected.

Oxidation of Dimethyldithiolethane.—The dimethyldithiolethane required was obtained very conveniently by methylating dithioglycol with methyl sulphate and aqueous alkali. To the disulphide (10 g.), dissolved in glacial acetic acid (100 c.c.) and cooled, hydrogen peroxide (20 g. of 29·2% aqueous solution) was added, and the mixture kept for 24 hours. The solution was then evaporated twice with addition of water, and the residue (12·5 g.) of mixed disulphoxides fractionally crystallised from ethyl alcohol, a mixture of ethyl alcohol and ethyl acetate (1 : 1), and finally from toluene or xylene. Two disulphoxides were thus separated, of which the α-isomeride was obtained pure more easily, as it was present in the larger quantity.

α-Dimethylethylenedisulphoxide crystallises from ethyl alcohol in monoclinic needles, m. p. 163—164° (Found: C, 31·1; H, 6·5; *M*, cryoscopic in camphor, 159. $C_4H_{10}O_2S_2$ requires C, 31·2; H, 6·5%; *M*, 154). It is readily soluble in water and moderately easily soluble in cold ethyl acetate or hot xylene.

β-*Dimethylethylenedisulphoxide* crystallises from alcohol or ethyl acetate in monoclinic bipyramids, m. p. 128—130° (Found: C, 31·0; H, 6·7%; *M*, 145). It is readily soluble in water or ethyl alcohol and sparingly soluble in ethyl acetate or hot toluene. The solubilities of the two isomerides in ethyl acetate at laboratory temperature are: α-, 0·16 g./100 c.c. (of solution); β-, 0·42 g./100 c.c. The melting point of the β-compound is not depressed by the addition of a little of the α-compound, although such mixtures have a considerable melting interval instead of a sharp melting point.

THE UNIVERSITY, SHEFFIELD. [*Received, May 17th,* 1927.]

CCXXXVI.—*Decomposition of some Halogenated Sulphides, and the Nature of the "Polymeric" Ethylene Sulphides.*

By ERNEST VERE BELL, GEORGE MACDONALD BENNETT, and ALFRED LOUIS HOCK.

THE union of an alkyl halide with an alkyl sulphide to produce a sulphonium salt is a reversible reaction, and unsymmetrical sulphonium halides may thus dissociate to yield compounds distinct from those used in their preparation:

$$R_2S + R'I \rightleftharpoons [R_2R'S]I \rightleftharpoons RR'S + RI$$

(Cahours, *Ber.*, 1875, **8**, 825; Klinger and Maassen, *Annalen*, 1889, **252**, 241).

An exactly analogous change was detected in an examination of some δ-substituted sulphides (this vol., p. 477) when a δ-bromobutyl sulphide was found to be transformed by internal salt formation into a cyclic sulphonium salt, $\left[\begin{matrix}CH_2\cdot CH_2\\ \\ CH_2\cdot CH_2\end{matrix}\!\!>\overset{+}{S}\cdot C_4H_8\cdot OH\right]Br$, which dissociated, on heating, with liberation of the cyclic tetramethylene sulphide:

$$Br\cdot R - R - S\cdot R' \rightleftharpoons \left[\begin{matrix}R\\ \\ R\end{matrix}\!\!>\overset{+}{S} - R'\right]Br \rightleftharpoons \begin{matrix}R\\ \\ R\end{matrix}\!\!>S + R'Br.$$

It appeared probable that a similar tendency to the formation of sulphonium salts by self-addition would be a property common to all classes of halogenated sulphides. No such tendency has hitherto been recognised, but we find that some observations of our own on β- and γ-halogenated sulphides and one or two anomalies recorded in the literature may be explained as the results of such processes of reversible sulphonium salt formation.

The self-addition of a halogenated sulphide might evidently be intermolecular or intramolecular. The latter type of reaction involves ring closure, and it may be anticipated that it will only be in evidence when a five- or six-membered ring is concerned, as in the case of the δ-bromo-sulphide. An indication of intermolecular addition in a γ-halogenated sulphide was obtained when γγ′-dichlorodipropyl sulphide was converted by the action of sodium iodide into the corresponding di-iodo-sulphide. The latter decomposed, on keeping, with liberation of trimethylene iodide in quantity, whilst a dark, viscous material was deposited which contained ionic iodine and was probably a mixture of complex substances. This may be explained as follows:

$$2S(C_3H_6I)_2 \rightleftharpoons \left[\begin{matrix}\overset{+}{S}(C_3H_6I)_2\\ \\ C_3H_6\cdot S\cdot C_3H_6I\end{matrix}\right]I \rightleftharpoons \begin{matrix}S\cdot C_3H_6I\\ \\ C_3H_6\cdot S\cdot C_3H_6I\end{matrix} + C_3H_6I_2.$$

The more complex di-iodo-sulphide on the right may undergo further changes of the same kind so that a mixture of substances results.

It is known that most specimens of ββ′-dichlorodiethyl sulphide contain dithian (see, *e.g.*, Davies, J., 1920, **117**, 299), but the reason for its presence has never been elucidated. It has usually been regarded as an impurity introduced at the time of preparation, but there is now no doubt that the proportion of dithian in samples of dichlorodiethyl sulphide increases greatly with the time of keeping. The production of dithian can be explained as due to a series of

reactions involving both the intermolecular and the intramolecular type of addition, thus,

$$2S(C_2H_4Cl)_2 \rightleftharpoons \left[S<\begin{matrix}C_2H_4\cdot\overset{+}{S}(C_2H_4Cl)_2\\C_2H_4Cl\end{matrix}\right]Cl \rightleftharpoons S<\begin{matrix}C_2H_4\cdot S\cdot C_2H_4Cl\\C_2H_4Cl\end{matrix} + C_2H_4Cl_2$$

$$S<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>S + C_2H_4Cl_2 \rightleftharpoons \left[S<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>\overset{+}{S}\cdot C_2H_4Cl\right]Cl$$

ethylene dichloride being a second substance produced in the process. We have tested the truth of this scheme of reactions, as far as possible, and have directly confirmed the formation of both dithian and ethylene dichloride in quantity from pure dichlorodiethyl sulphide heated at 180° for 18 hours. A similar reaction doubtless occurs more slowly at the ordinary temperature. If these reactions are reversible at each stage (as shown), the action of ethylene dichloride upon dithian should conversely to some extent yield dichlorodiethyl sulphide, although the amount present in the final equilibrium mixture might be small. We find that dithian heated at 180° with an excess of ethylene dichloride yields a highly vesicant liquid, and the presence of dichlorodiethyl sulphide is proved by the isolation of the crystalline ββ′-diphenoxydiethyl sulphide (Helfrich and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1208).

The curious observation of Davies (*loc. cit.*) that potassium cyanide acts on dichlorodiethyl sulphide to furnish the dinitrile, $CN\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot CN$, is intelligible from the same point of view. This dinitrile is a by-product evidently derived from an intermediate mononitrile as follows:

$$2CN\cdot C_2H_4\cdot S\cdot C_2H_4Cl \rightleftharpoons \left[\begin{matrix}CN\cdot C_2H_4\cdot\overset{+}{S}\cdot C_2H_4\cdot S\cdot C_2H_4\cdot CN\\C_2H_4Cl\end{matrix}\right]Cl \rightleftharpoons C_2H_4(S\cdot C_2H_4\cdot CN)_2 + C_2H_4Cl_2.$$

The formation and dissociation of a sulphonium salt also explains the anomaly noticed by Clarke (J., 1912, **101**, 1794) in the reaction of phenacyl bromide with dithian. The amount of ionic bromine, observed at intervals by titration, was found to rise at first as expected, but then diminished rapidly. This is clearly evidence of the opening of a ring as follows,

$$S<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>S + COPh\cdot CH_2Br \rightleftharpoons \left[S<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>\overset{+}{S}\cdot CH_2\cdot COPh\right]Br \rightleftharpoons S<\begin{matrix}C_2H_4\cdot S\cdot CH_2\cdot COPh\\C_2H_4Br\end{matrix}$$

the bromo-sulphide on the right containing no ionic bromine.

The Nature of the "Polymeric" Ethylene Sulphides.—The reactions

discussed above throw a new light on the nature of the "polymeric" ethylene sulphides, which are produced in a variety of reactions, such as the action of alkali sulphides on ethylene dichloride, ethylene dibromide or dichlorodiethyl sulphide, and by the dehydration of monothioethylene glycol. It is probable that they are all mixtures of substances of high molecular weight having a long open-chain structure of the type $A(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}B$, where A and B may be such groups as $-C_2H_4{\cdot}OH$, $-CH{:}CH_2$, or $-C_2H_4Br$ (Bennett and Whincop, J., 1921, **119**, 1861; *Nature*, 1926, **118**, 555; compare Staudinger, *Helv. Chim. Acta*, 1925, **8**, 67). The composition of these products is approximately that of a polymeride of ethylene sulphide (as is required by the formula provided that n be large), but it has long been known that variable amounts of bromine may be present (Crafts, *Annalen*, 1863, **128**, 220). The recent observations of Sir P. C. Rây and K. C. Bose-Rây (*J. Indian Chem. Soc.*, 1926, **3**, 75) support the idea of the occurrence of such long-chain bromopolyethylene polysulphides.

Two classes of "polymeric" ethylene sulphides were clearly distinguished by V. Meyer (*Ber.*, 1886, **19**, 3262): I, those which when heated did not yield dithian, and II, those which were readily degraded to dithian when heated alone or in solution in various solvents at high temperatures. The latter type of behaviour is to be expected in a bromo-polysulphide, owing to internal self-addition according to the scheme

$$R(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4Br \rightleftharpoons \left[R(S{\cdot}C_2H_4)_n{-}\overset{+}{S}\!<\!\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\!>\!S\right]Br$$

$$\Downarrow$$

$$R(S{\cdot}C_2H_4)_n{\cdot}Br + S\!<\!\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\!>\!S,$$

and repetitions of the process will liberate successive molecules of dithian, each cycle of changes being analogous to the reactions involved in the decomposition of dichlorodiethyl sulphide.

The existence of the "polymerides" of class I and their failure to yield dithian by a similar process will evidently be accounted for if they contain no halogen, since this is indispensable to sulphonium salt formation, and we find that, as far as evidence is available, "polymerides" which do not contain halogen do in fact belong to this class. Thus the material of Löwig and Weidmann (*Annalen*, 1840, **36**, 321) was found by Crafts (*loc. cit.*) to be free from halogen and to give no dithian on heating. We have confirmed the complete absence of halogen from a specimen of "polymeride" of class I prepared from ethylene dibromide, whilst products of class I from monothioethylene glycol were made from halogen-free materials

(J., 1922, **121**, 2144). These facts support our suggestion that it is the absence or the presence of halogen which determines the chemical differences between " polymerides " of class I and class II. In those of class I the terminal groups in the molecule are probably either $-C_2H_4\cdot OH$ or $-CH{:}CH_2$. Such substances would be likely to react with hydrogen bromide or with ethylene dibromide to yield halogenated polysulphides by such reactions as the following:

$R\cdot S\cdot C_2H_4\cdot OH + HBr = R\cdot S\cdot C_2H_4Br + H_2O$; $R\cdot S\cdot CH{:}CH_2 + HBr = R\cdot S\cdot C_2H_4Br$; $R\cdot S\cdot R' + C_2H_4Br_2 = R\cdot S\cdot C_2H_4Br + R'Br$.

The products would then be liable to the process of degradation with liberation of dithian. This anticipation also has been verified: " polymerides " of class I yield dithian when heated in boiling phenol, provided that hydrogen bromide or ethylene dibromide be added.

The simpler substances $S(C_2H_4\cdot OH)_2$, $C_2H_4(S\cdot C_2H_4\cdot OH)_2$, and $S(C_2H_4\cdot S\cdot C_2H_4\cdot OH)_2$ previously described (Bennett and Whincop, *loc. cit.*), which are not easily decomposed when heated alone, have now been found, as expected, to yield dithian readily when they are heated with a boiling solution of hydrogen bromide in phenol. These three dihydroxy-sulphides are the simplest members of a homologous series of substances, the higher members of which are doubtless present in " polymeric " ethylene sulphides of class I.

Experimental.

Action of Sodium Iodide on γγ'-Dichlorodipropyl Sulphide.—The pure dichloro-sulphide was heated in acetone solution with sodium iodide (3 mols.) until sodium chloride was no longer precipitated. The solution was concentrated, and the crude *γγ'-di-iododipropyl sulphide* thrown out as a heavy oil by dilution. This substance did not crystallise and could not be distilled without decomposition. When kept for several weeks at the ordinary temperature, the liquid deposited a dark resinous material which slowly hardened, but retained pockets of a heavy mobile oil. The solid could not be crystallised; it was partly soluble in water, the solution containing ionic iodine.

The oil was separated, and distilled at 120—130°/50 mm. It was identified as trimethylene di-iodide by direct comparison and by its ready conversion on heating with a solution of sodium phenoxide in phenol into αγ-diphenoxypropane, of which the m. p., 59—60°, was unaltered by admixture of an authentic specimen.

Decomposition of ββ'-Dichlorodiethyl Sulphide.—Freshly redistilled dichlorodiethyl sulphide (2·5 g.) was heated in a sealed tube for 18 hours in the vapour of boiling phenol. When the tube was

opened, a volatile liquid was noticed. The contents of the tube were mixed with an excess of aniline and heated at 100° for an hour and then at the boiling point for a further hour. The excess of aniline and the dithian were removed in a current of steam and the distillate was acidified to dissolve the aniline. The precipitate (0·5 g.; 50% of the theoretical yield) had m. p. 111°, not depressed by admixture of pure 1 : 4-dithian.

The residue from the steam distillation was extracted with ether, and the ether evaporated. The residual oil gave a crystalline sulphate when warmed with sulphuric acid (50%). This salt was crystallised from the filtered solution, and the base liberated from it by ammonia was crystallised from paraffin (b. p. 60°) and identified as ethylenediphenyldiamine, m. p. 60°, not depressed by admixture of an authentic specimen. This proves that the tube must have contained ethylene dichloride when opened.

The Action of Ethylene Dichloride upon Dithian.—Dithian (0·5 g.) and ethylene dichloride (5 c.c.) were heated in a sealed tube for 12 hours at 180°. Evaporation of the ethylene dichloride left a brown oil, which had a strong vesicant action. It was heated with an excess of alcoholic sodium phenoxide, and the solution was acidified and distilled in steam. The residual oil was removed in ether, and the latter evaporated. The viscous residue deposited crystals, which were drained on porous earthenware and recrystallised from paraffin of low b. p. This substance had m. p. 54°, not depressed by admixture of an authentic specimen of ββ′-diphenoxydiethyl sulphide. The two substances were also found by microscopic examination to crystallise identically from ethyl alcohol in bunches of needles with a straight extinction.

Degradation of "Polymeric" Ethylene Sulphide of Class I.—The specimen of "polymeride" was made by the action of alkali sulphide on ethylene dibromide, and had been freed from all trace of "polymeride" of class II by heating in phenol. It gave no dithian when dry-distilled or when heated in boiling phenol for several hours. Repeated tests proved the absence of halogen from this material.

The "polymeride" (30 g.) was heated at 130° for 1 hour with ethylene dibromide (18 g.; 1/5 mol.). Phenol (60 g.) was then added, and the mixture boiled for 3 hours. Addition of an excess of aqueous sodium hydroxide left a crystalline precipitate identified as dithian (6·7 g.).

The "polymeride" (15 g.) was boiled for 2 hours with phenol (60 g.) saturated with hydrogen bromide, and dithian was isolated as before (5 g.).

Production of Dithian from Simpler Hydroxy-sulphides.—Thio-

diglycol, ethylenebis-β-hydroxyethyl sulphide, and sulphidobis-β-hydroxydiethyl sulphide were each boiled for 2 hours with phenol saturated with hydrogen bromide, and the mixture was separated as before. In each case, dithian was identified, the yield from the last-named substance being nearly 50% by weight.

THE UNIVERSITY, SHEFFIELD. [*Received, May 31st*, 1927.]

CCXXXVII.—*Colour and Molecular Geometry. Part V. A Search for a Crucial Test of Colour Theories.*

By JAMES MOIR.

ANY theory of colour must, to be really successful, cover the whole field of absorbing substances—and this not merely qualitatively but quantitatively. It is not sufficient, for example, to establish a scheme in which most "coloured" (*i.e.*, absorbing) substances can be formulated with a little manipulation as "quinonoid" or as possessing alternate double and single linkages, inasmuch as there are plenty of exceptions to these schemes, namely, cases in which the amount of manipulation of the formula required to make it quinonoid is beyond belief (for example, *m*-aminophenol) or even beyond possibility (for example, the coloured solution of dihydroanthracene in concentrated sulphuric acid). It is also not sufficient to establish a scheme in which the various absorption bands of a substance examined in different media are related to one another in the same way as harmonics of a fundamental tone are, inasmuch as the connexion between the value of the fundamental and the chemical constitution has still to be discovered, also the reason why unexpected harmonics such as the 19th appear. A 19th harmonic is only credible if accompanied by the 7th, 13th, and 25th, or similar series; in other words, prime numbers as harmonics require a special explanation.

The author's theory, whilst admittedly a makeshift, is the only one capable of giving predictions of colour from constitution. Its use, however, is very greatly restricted by our lack of knowledge of the actual dimensions of many common molecules. Even the true configuration of benzene is still in doubt,* although the relation between anthracene and naphthalene is considered to be beyond doubt.

* Many writers appear to think that Körner's model is the same as Bragg's—which is not the case. The angle between adjacent carbon atoms in the skew-hexagon is 109° in Bragg's model and 90° in Körner's; consequently the representation of the position of the hydrogen atoms in Körner's model is quite erroneous.

The author therefore presents in this paper an experimental study of some of the oxygen derivatives of anthracene (together with a few of the corresponding derivatives of naphthalene) with the view of providing data for a crucial test of his own and other colour theories, a test founded on the fact that there is hardly any dispute as to the size and spatial configuration of the anthracene and naphthalene molecules.

Tables I and Iᴀ contain the author's observations of the positions of the bands of these oxygen derivatives, made in dilute aqueous sodium hydroxide solution, in presence of sodium sulphite to prevent aërial oxidation.

TABLE I.

Absorption of Hydroxy-derivatives of Anthracene in Excess of Alkali.

	Central λ (in $\mu\mu$) of chief band.	Fainter bands.
1-Hydroxy-9 : 10-dihydroanthracene *	312	Nil.
1-Hydroxyanthracene (α-anthrol)	364	347, 410 broad
2-Hydroxyanthracene (β-anthrol)	335	Nil.
9-Hydroxyanthracene (anthranol)	378	,,
1 : 9-Dihydroxyanthracene (α-hydroxyanthranol)	490	460
2 : 9-Dihydroxyanthracene (β-hydroxyanthranol A)	476	447
3 : 9(or 2 : 10)-Dihydroxyanthracene (β-hydroxyanthranol B)	510	480
1 : 5-Dihydroxyanthracene (rufol)	371	354, 420 broad
2 : 6-Dihydroxyanthracene (flavol)	345	312, 378 broad
2 : 7-Dihydroxyanthracene	390	Nil.
9 : 10-Dihydroxyanthracene (anthraquinol)	495 broad	,,
1 : 5 : 9-Trihydroxyanthracene (anthrarufinanthranol)	427	370
1 : 2 : 10-Trihydroxyanthracene (deoxyalizarin)	480	Nil.
2 : 6 : 9-Trihydroxyanthracene (anthraflavinanthranol)	416	490, 515
2 : 7 : 9-Trihydroxyanthracene (*iso*anthraflavinanthranol)	492	466
2 : 9 : 10-Trihydroxyanthracene (β-hydroxyanthraquinol)	575	685
2 : 6 : 9 : 10-Tetrahydroxyanthracene (hydroanthraflavin)	486	454
1-Hydroxyanthraquinone	480	500
2-Hydroxyanthraquinone	470	495
1 : 2-Dihydroxyanthraquinone (alizarin)	613	568, 523
1 : 4-Dihydroxyanthraquinone (quinizarin)	595	552, 516
1 : 5-Dihydroxyanthraquinone (anthrarufin)	470	500
2 : 6-Dihydroxyanthraquinone (anthraflavin)	430	400, 485
2 : 7-Dihydroxyanthraquinone (*iso*anthraflavin)	475	390, 500

* The author finds that 1-hydroxy-9 : 10-dihydroanthracene (contrary to the statements of Liebermann, *Annalen*, 1882, **212**, 15, and Pleus, *Ber.*, 1902, **35**, 2928) is a phenolic substance closely resembling the cresols and has no colour in alkali. The author's specimen was made by sodium reduction of α-anthrol and agreed in appearance and melting point with the data in the literature.

TABLE Ia.

Absorption of some Corresponding Naphthalene Derivatives in Excess of Alkali.

	Central λ (in $\mu\mu$) of chief band.	Fainter bands.
1-Hydroxynaphthalene	330	Nil.
2-Hydroxynaphthalene	349	,,
1 : 5-Dihydroxynaphthalene	350	,,
2 : 6-Dihydroxynaphthalene	340	356
2 : 7-Dihydroxynaphthalene	338	393
5-Hydroxy-1 : 4-naphthaquinone (juglone)	510	570
5 : 6-Dihydroxy-1 : 4-naphthaquinone (naphthazarin)	619	571

TABLE II.

Sulphonates in Aqueous Alkali.

Name.	Position of bands.
Anthraquinone-1-sulphonate	340 and 385
Anthraquinol-1-sulphonate	493 and 515
Anthranol-1-sulphonate	385 and 363
Anthracene-1-sulphonate	383, 364, 345, 326, and 308
Anthraquinone-1 : 5-disulphonate	333 and 420
Anthraquinol-1 : 5-disulphonate	491, 533, and 590
Anthranol-1 : 5-disulphonate	432, 460, and 490
Anthracene-1 : 5-disulphonate	389, 370, 350, and 305

The first point to be noted from the observations is the very interesting one that both of the anthrols and both of the symmetrical anthradiols are *visibly* coloured in moderately concentrated (N/500) solution, whereas the corresponding derivatives of naphthalene, all of which have absorption bands situated below λ 390 (the usually accepted lower limit of human vision), are not coloured in alkaline solution unless the solutions are very concentrated (over N/10). The α-compounds are more highly coloured than the β-compounds.

The second point is that the behaviour of the 1 : 5-dihydroxy-compounds is almost the same as that of the 1-hydroxy-compounds and that the 2 : 6-dihydroxy-compounds resemble the 2-hydroxy-compounds in behaviour. This symmetry clearly points to an influence of the centre (or the central plane) of the molecule on the height of colour.

The third point is the high colour (λ above 470) produced when one hydroxyl group is present in the 9-position. All the anthranols and anthraquinols show this, and, as is well known, all the hydroxyanthraquinones can be formulated in an alternative form with an OH-group in position 9. Usually the anthranol has a similar colour to that of the anthraquinone. This high colour is not easy to explain on any theory of colour.

The fourth point is that the highest colours of all occur in 2 : 9 : 10-, 1 : 2 : 9 : 10-, and 1 : 4 : 9 : 10-compounds (the 1 : 9 : 10-compound, α-hydroxyanthraquinol, could not be obtained). This is evidently due to superposition of effects due to the 9 : 10 arrangement—in itself capable of giving a red colour—on effects due to the co-operation of hydroxyl and the anthracene skeleton—in itself capable of giving a yellow colour, as shown above.

The last point is that the phenomena are almost exactly duplicated in the naphthalene series, so that the third ring in anthracene is of little significance. Thus juglone resembles erythrohydroxyanthraquinone, naphthazarin resembles alizarin, and all the mono- and di-hydroxynaphthalenes examined resemble the corresponding derivatives of anthracene. Nevertheless, anthraquinol (red in alkali) does not closely resemble 1 : 4-dihydroxynaphthalene in colour, although the alkaline solution of the latter compound is yellow (in presence of reducing agents to avoid oxidation), in contradistinction to that of ordinary quinol. 9 : 10-Anthraquinol in alkali absorbs from λ 520 to λ 470, 1 : 4-naphthaquinol at about λ 400, and quinol at λ 316.*

Those who have followed the author's attempts to find a theory of colour will remember that six years ago he put forward a factorial scheme whereby 90% of the data for dicyclic coloured substances could be correctly predicted (J., 1921, **119**, 1654), and later he showed that alteration of the angle between the rings is the reason why dicyclic coloured substances linked by carbon have lower colours than the corresponding substances in which nitrogen or oxygen forms the joint between the rings.

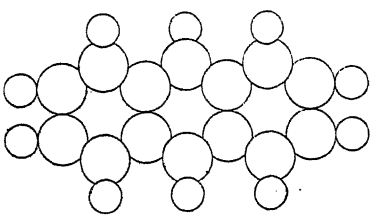
Further consideration shows that this scheme must sometimes break down when there is more than one joint, and this merely because the two joints cannot approach one another closely when one of them is carbon with its comparatively severe bend of 109°. Consequently, the calculated values for dihydroxyxanthhydrol and dihydroxyacridine are slightly incorrect (−3%), whereas those for dihydroxyanthracene, dihydroxyacridone, and dihydroxyxanthone are seriously incorrect (−12 to −25%). This means that the factor 0·65 used for calculating linkage by carbon can only be used once, so that if there is linkage by a second atom (in the ortho-position to the first linkage, of course) it occurs in such a way as to keep the molecule as flat as possible. Bragg's model for anthracene is an example, for, if my 1921 theory had been entirely correct, the anthracene model resulting would have been "buckled" in the

* If these effects are merely due to "loading" of quinol with one or with two benzene rings respectively, they are much the largest loading effects known.

middle, this being the only way in which both the central carbon atoms could make the normal (109°) angle with both rings.

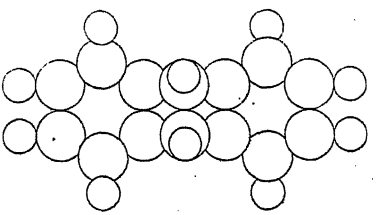
Figs. 1 and 2 represent two possible ways in which Bragg's measurements may be satisfied without any "buckling." Fig. 1, being without a cross bond, really represents dihydroanthracene, but is Bragg's own original diagram, with the β-hydrogen atoms put in the same plane as the β-carbon atoms. Fig. 2 shows the cross bond of anthracene as part of a Dewar–Ingold benzene model (triangular prism). Both models measure 11·18 Å. by 6·00 Å. The dimension 11·18 Å. of anthracene is made up of two ordinary benzene rings each of width 2·57 Å., one central ring of width 2·50 Å., two halves of a carbon atom, equal to 1·54 Å., and two hydrogen atoms, equal to 2·00 Å. The other dimension (vertical) is made up of $2{\cdot}57 \div (\sqrt{3}/2)$ (from the properties of a hexagon), plus two halves of a carbon atom, plus the projection of two hydrogen atoms lying

Fig. 1.



Anthracene (Bragg).
Dihydroanthracene (Moir).

Fig. 2.



Anthracene (Moir).

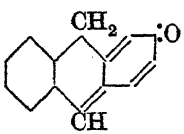
at 109° to the plane of the paper containing the β-carbon atoms. Similarly, if the middle ring be removed, the diagram agrees exactly with that of naphthalene [$(2 \times 2{\cdot}57) + (2 \times 0{\cdot}77) + 2{\cdot}0 = 8{\cdot}68$ for the length, whilst the breadth remains at 6·00 as in anthracene], these dimensions being exactly those given by Bragg. Inferentially also, the dimensions of the benzene molecule become, in this scheme, 6·11 Å. × 6·00 Å., a much closer approach to a true hexagon than one would expect at first sight from a molecule possessing a carbon skeleton of the skew-hexagon nature prescribed by Bragg.

Application of the Model to the Author's Colour Theory.

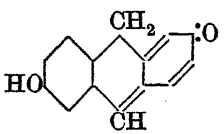
The extreme form of the author's theory, according to which the distance between the centres of the oxgyen atoms of the auxochromes decides the colour, is at once seen to be incorrect, because if this form of the theory were true, the substance flavol (2 : 6-dihydroxy-anthracene), in which the centres of the oxygen atoms are as far apart as possible (10·6 Å. on the model), would possess an absorption

band at λ 850. Similarly, 2 : 6-dihydroxynaphthalene, which has, on the model, a distance of 8·1 Å. between its oxygen centres, would have a band at λ 650. Observation shows that the position of the chief band of both these substances is practically the same (λλ 345 and 340 respectively), both being pale yellow in alkaline solution. Light is now thrown on this obscurity by the fact that β-anthrol and β-naphthol have similar absorptions when examined in alkali solution (λλ 335 and 349 respectively). This shows that the colour vibration (colour orbit on the author's theory) is not from auxochrome to auxochrome, but is from *one* (that is to say, from either) auxochrome to a centre of force near the centre of the molecule.

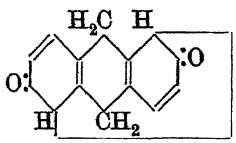
This idea can be correlated with the quinonoid theory as follows: β-Anthrol can be written as a quinonoid compound (I), and similarly flavol can be written as (II) but cannot be written so as to make the oxygens of *both* auxochromes quinonoid. I assume that such a formulation as (III) is patently absurd.



(I.)

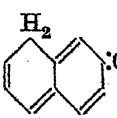


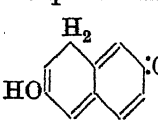
(II.)



(III.)

The cause of the band round about λ 340 in these four compounds (β-naphthol, 2 : 6-dihydroxynaphthalene, β-anthrol, and flavol) thus only concerns one ring. On my theory, λ 340 corresponds to a positive-centre distance of 4·36 Å. if both centres are oxygen atoms,* and about 4·2 Å. if one is a carbon atom. The latter distance on the model agrees with an orbit in which the electron grazes the oxygen atom of the auxochrome and at the other end of the ellipse passes through the double bond outside the para-carbon atom, the positive centres being the auxochrome oxygen and the para-carbon atom. Thus my theory leads to the same result as is reached by the quinonoid theory. The quinonoid formulæ for β-naphthol and 2 : 6-dihydroxynaphthalene involved are (IV) and (V), although they have also been formulated as ortho-quinonoid.

(IV.) 

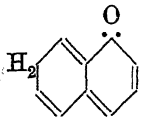
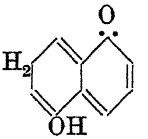
and 

(V.)

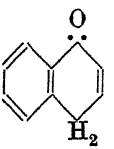
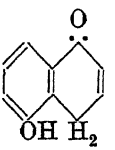
The α-compounds may now be considered. α-Naphthol and 1 : 5-dihydroxynaphthalene have much the same absorption as the

* For these calculations involving oxygen atoms alone, I find that the expression $\lambda = 82d - 20$ is sufficiently accurate.

β-compounds just discussed, *viz.*, an average value of 340 for λ. The corresponding distance is again 4·2 Å. and the corresponding quinonoid formulæ are :

(VI.)  and  (VII.)

Nevertheless, no distance can be found on the model in agreement with these suppositions. Agreement can, however, be obtained if the more customary quinonoid form be assumed, in which

(VIII.)  and  (IX.)

case the distance between oxygen and para-carbon agrees with what is required : the case thus becomes, in this instance, that of phenol with a "load."

The α-compounds of anthracene have a higher colour than those of naphthalene, due to bands at λλ 368 and 415 (on the average).

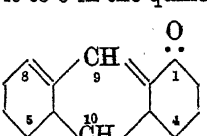
Alkaline solutions of 1-anthrol and of rufol (1 : 5-dihydroxy-anthracene) are yellow even in great dilution.

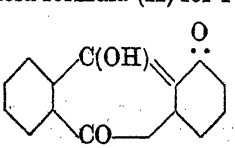
When, however, it comes to finding an explanation of this, it appears that Bragg's work is unfortunately less decisive as to the relative positions of α-groups than of β-groups.

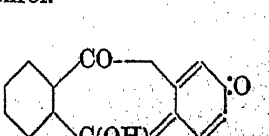
It is usually assumed, nevertheless (as on p. 1813), that α-groups lie in line with the benzene valencies, *i.e.*, inclined to the general plane of the model at the angle of 55° ($\sin^{-1}\sqrt{\frac{2}{3}}$) prescribed by the geometry of the skew-hexagon benzene model. An attempt to depict this *in plano* is shown in Figs. 1 and 2.

I find that an orbit round the α-oxygen and para-carbon atoms does not suit the colour, although the analogous supposition does suit in the case of the β-compounds. Neither does an orbit round the 1-α-oxygen and the 10-*meso*-carbon atom.

The only orbit which agrees is one which involves the double linkage lying between carbon atom 8 and its neighbour which links it to 9 in the quinonoid formula (X) for 1-anthrol.


(X.)


(XI.)


(XII.)

The centre of this unnumbered linking-carbon atom is at approximately the correct distance from the centre of the 1-oxygen atom to account on my theory for the observed band at λ 415 and the yellow colour.

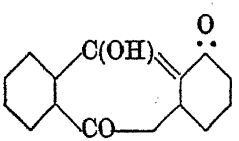
The Hydroxyanthraquinone Dyes.

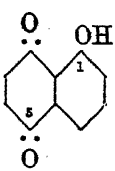
In explaining the colour of these dyes the author accepts the customary theory that the oxygen atoms attached at positions 9 and 10 compete with the hydroxylic oxygen atoms for a tautomerising hydrogen atom, as in the usual formulæ (XI and XII).

The tautomerism of the β-compounds is the ordinary quinonoid one, but in the α-compounds the chemical bonds cannot be arranged so as to show a tautomerism between 1- and 10-oxygens. This need not, however, deter us from conceiving the colour as being due to the movement of a single electron round these two oxygen atoms considered as positive centres—inasmuch as the case is similar to that of the "meta-quinonoid" coloured substances such as *m*-nitroaniline.

The distances, 6 Å. (α) and 6·5 Å. (β), between the centres of the oxygen atoms in question agree with what is required to explain bands occurring between λ 470 and λ 510. The *quinonoid* formula for erythrohydroxyanthraquinone (XIII) leads to a much smaller

(XIII.)





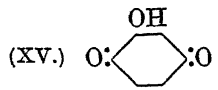
(XIV.)

distance (2·6 or 2·9 Å. according as the 1- and 9-oxygen atoms are on the same or opposite sides of the general plane of the molecule), a distance corresponding to bands between λ 215 and λ 240 in the low ultra-violet region. Meyer and O. Fischer (*Ber.*, 1913, **46**, 85), in the cases of 1-hydroxyanthraquinone and anthrarufin, observed no bands below λ 265, but the lower limit of their investigation was probably not low enough to reach bands situated at λ 220.

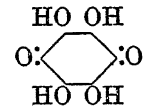
The cause of the colour of juglone (5-hydroxy-1 : 4-naphthaquinone, *i.e.*, 1-hydroxy-5 : 8-naphthaquinone) (XIV) and of 1-hydroxyanthraquinone is the same, an orbit round the oxygens attached in positions 1 and 5. The third ring in 1-hydroxyanthraquinone has no effect, as is seen also to be the case by comparison of the bands of naphthazarin with those of alizarin.

It is a curious fact, however, and one not easy to explain, that colour of this height (λ 480 or so) can arise in compounds of only *one* ring, such as hydroxybenzoquinone and tetrahydroxybenzo-

quinone, when examined in alkaline solution. This is nevertheless not strictly analogous, since in juglone the hydroxyl group is



(XV.)



(XVI.)

attached, not directly to the quinone ring, but to a carbon atom attached to that ring. Probably a special explanation, similar to that of the high colour of alizarin (see below), is called for here.

The colour of anthrarufin is explained in the same way as that of 1-hydroxyanthraquinone, and the colour of anthraflavin and of *iso*anthraflavin in the same way as that of 2-hydroxyanthraquinone (see p. 1816).

The high colour of alizarin and naphthazarin constitutes part of a general phenomenon seen also in benzeneazopyrocatechol, 3 : 4-dihydroxybenzophenone, etc., whereby the presence of two hydroxol groups adjacent to one another greatly heightens the colour (Table III).

TABLE III.

Substance.	λ.	Comparison substance.	λ.
Benzeneazopyrocatechol ...	480	Benzeneazophenol	433
Phenolpyrocatechol-phthalein	579	Phenolphthalein	554
Pyrocatecholphthalein	652		
o-Hydroxyfluorescein	523+498	Fluorescein	494+457
oo'-Dihydroxyfluorescein ...	550+527		
3 : 3' : 4 : 4'-Tetrahydroxy-benzophenone	449+406	4 : 4'-Dihydroxybenzo-phenone	323

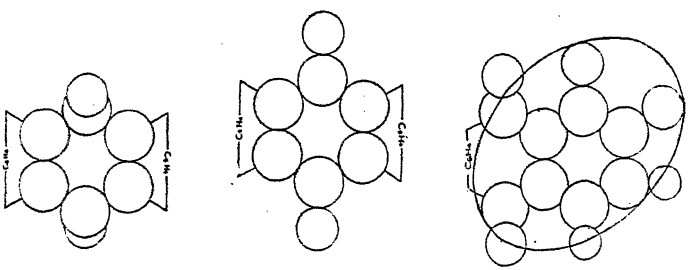
I am of opinion that the explanation is that the electron goes round *both* of the ortho-oxygen atoms as well as the third (distant) oxygen atom (Fig. 5), and thus describes an ovoid orbit which is wider than the normal type of colour ellipse (see J., 1922, **121**, 1810). This connotes a longer path and longer periodic time and higher colour, the eccentricity of the ellipse having been increased. The essential idea in this explanation of the heightening effect of contiguous auxochromes is that the two atoms behave (as in ordinary mechanics) as if their forces were condensed into their "centre of gravity" (the point midway between them), whilst the moving electron has to *touch the outsides* of both of them and so is constrained to move in one plane and thus give an ovoid orbit slightly wider at one end than at the other. In simpler coloured substances, of course, the orbit round two positive centres may be in almost any plane.

The hydroxyanthracenes and the hydroxyanthraquinones having been disposed of, it remains to discuss the colours of the hydroxyanthraquinols and hydroxyanthranols.

(*a*) Anthraquinol itself (in alkali) has a much higher colour than anthraquinone, a phenomenon *sui generis*, since it does not occur in the benzene and naphthalene series, in which the quinol has a lower colour than the quinone. It can only be explained on my theory by supposing the central ring flattened and the two (9 and 10) hydroxyl groups attached outside in the same plane. In this way, the oxygen atoms can be sufficiently separated to agree with the theory and the observed colour (see Table I). In anthraquinone, however, the theory requires that the distance between the oxygen atoms shall be only two-thirds of that required for anthraquinol; this agrees with the ordinary buckled-ring structure. Figs. 3 and 4 represent anthraquinone and alkaline anthraquinol according to the theory.

It is difficult to investigate the hydroxyanthraquinols on account of their great liability to oxidation, but they appear to have even

FIG. 3. FIG. 4. FIG. 5.



Anthraquinone. *Ionised anthraquinol.* *Colour-orbit in alizarin.*

higher colours than anthraquinol, requiring for explanation the ovoid orbit round oxygen atoms situated in the 1 : 9 : 10 and 2 : 9 : 10 positions.

(*b*) The hydroxyanthranols all have much the same colour as anthraquinol, intermediate in "height" between those of the corresponding hydroxyanthracenes and hydroxyanthraquinones. Those of the 1 : 10 and 2 : 10 type have slightly higher colours than those of the 1 : 9 and 2 : 9 type (see Table I). The explanation of their colour on my theory is that the distance between the oxygens is intermediate between that for the hydroxyanthracenes and that for the hydroxyanthraquinones, both of which have been accounted for above.

This shorter distance is accounted for by the fact that the central hydroxyl group of the anthranols is attached in the same way as the *meso*-hydrogen atoms of anthracene. It is thus plain from Fig. 2 that the distance from this hydroxyl to an α- or β-hydroxyl is less than in the case of the hydroxyanthraquinones.

Part II.

Some reference to the views expressed in the Report of the British Association Committee on Spectra and Constitution (1922) is called for from one who still believes that there is a relationship between chemical constitution and the position of absorption bands.

It is, of course, true that the portion of the field of ethereal vibration concerned with colour is less than one five-thousandth of the whole field. The author has, however, shown that the *whole* of the substances chemically related to a single parent substance possessing a band in this minute fraction of the possible field have also a band or bands in this same tiny region (J., 1923, **123**, Tables from p. 2797 to 2803), a fact which if ascribed to coincidence is incredible, but if ascribed to "loading" of the parent substance is eminently reasonable. For example, it appears to be impossible to make any derivative of azobenzene which shall not have a band somewhere between λ 420 and λ 600.

Again, the harmonic results for the anthracene family could be simplified if it is admitted that such of the observations as were made in concentrated sulphuric acid are not directly comparable with those made in alkali. Every such observation should be corrected for the very considerable "loading" effect of the solvent, in the same way as observations in alcohol must be corrected for comparison with observations in water, whereupon the bands coincide.

The case of benzene as studied by McVicker, Marsh, and Stewart is particularly interesting on account of the very definite harmonics arrived at (J., 1923, **123**, 642, 817, 2147). The heads of the Tesla bands were found to be the 33rd, 34th, 35th, 36th, 37th, 38th, and 39th harmonics of a fundamental in the infra-red at $\nu = 987{\cdot}1$ vibrations per cm.* ($\lambda = 10131$ μμ).

The 36th harmonic ($\nu = 35540$, $\lambda = 281\frac{1}{2}$) is the strongest. There is also a fine structure of subsidiary bands, making probably 84 in all between λ 310 and λ 260, all expressible as submultiples of the fundamental (considered as a double band of λλ 10131 and 10162) thus: $\nu = \left\{\begin{matrix}987{\cdot}1\\983{\cdot}6\end{matrix}\right\}\left(1 \pm \frac{n}{216}\right) \times$ harmonics.

Combining this discovery with the knowledge of the positions of two *observed* infra-red bands of benzene at about λλ 1680 and 6750 μμ, we find that we must either assume the real fundamental λ of benzene to be twice that given above (20260 μμ, $\nu = 493{\cdot}5$), in which case the harmonics go up to No. 78; or else keep to the result given above, with no harmonic higher than 39, and explain the band at 6750 μμ by a special hypothesis.

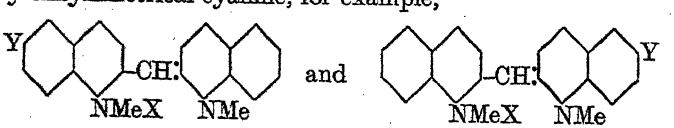
* Stated as 98·71 in their paper, different units being used.

It is fairly clear, however, from the mass of evidence brought forward by Deslandres and referred to later on, that absorption bands possessing a fine structure are caused by the nuclei of the atoms of the molecule and not by the atoms or by the molecule itself.

Part III. Stieglitz's Theory.

Stieglitz, on the contrary, believes with me that there is a connexion between colour and chemical structure or constitution. He has put forward a geometrical theory of the same character as mine (Franklin Institute Centenary Address, 17th September, 1924; *Proc. Amer. Chem. Soc.*, 1920, **43**, 36), but differing fundamentally in that an electron orbit is assumed round *one* atom, but disturbed by the proximity of a second positive centre. The orbit, according to Stieglitz, is not an ellipse round the two positive centres, but is a Cassinian oval round *one* of them, apparently exactly as in Morgan's theory of combination, the electrons being never sufficiently disturbed to become governed by two nuclei (see *Chem. and Industry*, 1924, 1071). A diagram is given there which in my opinion explains the whole subject, not only of chemical combination, but also of absorption and colour. The inner Cassinian ovals (3 in number in Morgan's figure) represent some of the Bohr orbits as disturbed (but not seriously altered) by the proximity of a second positive centre; they represent what happens when electrons are affected by radiation when the second positive centre is distant. The outer ellipse, on the other hand, is the orbit suggested by the present author to explain colour and involves a comparative proximity of two ionised positive nuclei, so that the electron is completely displaced from one and can go round both. An intermediate stage is shown by the permanganate, uranyl, uranous, neodymium, erbium, and praseodymium ions, in which rhythmically related bands occur, but no fine structure in the bands. This is just possibly connected with the intermediate lemniscate orbit.

Stieglitz's theory has not yet had its mathematics worked out and therefore cannot be tested quantitatively against my own, but he produces one case which is inconsistent with my theory (and also inconsistent with the theory of tautomerism), *viz.*, the existence of two distinct dimethylmurexides, one of which is alloxandimethyluramilazomethine and the other dimethylalloxanuramilazomethine. Similarly, on Stieglitz's theory there should be two isomeric forms of every unsymmetrical cyanine, for example,



In Stieglitz's theory, which is founded on the general principle of $\alpha\gamma$-tautomerism, the carbon atom adjoining but outside a double bond is the one round which the perturbed oval orbit is performed by an electron; and the other positive centre is the farthest-away atom of the doubly bonded pair.

Stieglitz's theory gives a better explanation than mine of such problems as the colour of nitrosobenzene, sodium-benzophenone, and other metal-ketyls, and Wieland's substances with bivalent and quadrivalent nitrogen.

Part IV. Deslandres's Theory.

H. Deslandres propounds a law among infra-red absorptions of simple substances whereby they are all connected together, whatever the observed substance may be. He expresses it (*Compt. rend.*, 18 May, 29 June, 17 Aug., and 28 Sept., 1925) in the form $\nu = d_1 q/rs$, in which d_1 is a universal constant or frequency ($1062\frac{1}{2}$ vibrations per cm.), q is the harmonic number of the particular band, r is the number of "octets" in the compound, one being assigned to each hydrogen,* and s is a vulgar fraction (*usually greater than unity*), the value of which is irregular and has not yet been connected with the chemical constitution either of the molecule or of its atoms.

Deslandres's formula can of course be also written: $\lambda = krs/q$, in which q, r, and s are as just defined, but $k = 9412$ $\mu\mu$ when λ is expressed in $\mu\mu$.

Deslandres ascribes the origin of his universal constant to vibration of the α-particle contained in all higher atomic nuclei. This vibration in the nucleus is supposedly synchronous with the irregular motion of the electron in the ovoid orbit suggested by Morgan (see p. 1820).

I have nevertheless thought it interesting to work out what the values of the vulgar fraction are in the compounds discussed at the beginning of the paper.

In constructing the following table the total variation of the constant has been kept less than $\pm \frac{1}{2}\%$, so as to fix the vulgar fraction. The vulgar fractions resulting are *wholly erratic and disconnected*, and therefore have no real existence.

Benzene gives $\nu = 1066/12 \times 100/9 \times$ (harmonics, *viz.*, 6, 33, 34, 35, 36 ... 39) for the brighter bands and $\nu = 1062\frac{1}{2}/12 \times 100/9 \times$ (harmonics) for the satellites. Here 12 is the value of r; and the vulgar fraction s is 9/100. Henri's vapour-absorption results (*J. Phys. Radium*, 1922, 181) give the fraction as 12/125.

Pyridine gives $\nu = 1066/11 \times 5/3 \times$ (harmonics). Here 11 is the value of r and the vulgar fraction is 3/5.

* *E.g.*, five, not one, in methane: three in water, four in hydrogen sulphide and five in carbon disulphide.

Anthracene gives two alternative results, *viz.*,
(*a*) $\nu = 1066\frac{1}{2}/24 \times 9/8 \times$ (harmonics from 53 to 82), or
(*b*) $\nu = 1060/24 \times 10/3 \times$ (harmonics from 18 to 22); plus
$\nu = 1065{\cdot}3/24 \times 16/5 \times$ (harmonics from 19 to 24).
Naphthalene gives $\nu = 1064/18 \times 14/9 \times$ (harmonics from 34).
Anthraquinone gives $\nu = 1064\frac{1}{2}/24 \times 50/11 \times$ (harmonics from 12).
Dihydroanthracene gives $\nu = 1061/26 \times 35/4 \times$ (harmonics from 7).
Anthranol gives $\nu = 1064\frac{1}{2}/25 \times 29/14 \times$ (harmonics from 29).
1-*Anthrol* gives $\nu = 1067/25 \times 23/15 \times$ (harmonics from 36).
2-*Anthrol* gives $\nu = 1066/25 \times 35/8 \times$ (harmonics from 14).
Anthraquinol gives $\nu = 1066/26 \times 60/17 \times$ (harmonics from 11).
2-*Hydroxy*-9-*anthranol* gives $\nu = 1067/26 \times 16/5 \times$ (harmonics from 16).
3-*Hydroxy*-9-*anthranol* gives $\nu = 1063/26 \times 3/1 \times$ (harmonics from 16).
Naphthazarin gives $\nu = 1064/20 \times 38/15 \times$ (harmonics from 12).
Alizarin gives $\nu = 1060/26 \times 5/3 \times$ (harmonics from 23).
Quinizarin gives $\nu = 1065/26 \times 4/1 \times$ (harmonics from 10).
Anthrarufin gives $\nu = 1064/26 \times 11/9 \times$ (harmonics from 35).
Rufol gives $\nu = 1062\frac{1}{2}/26 \times 11/7 \times$ (harmonics from 36).
Flavol gives $\nu = 1060/26 \times 40/9 \times$ (harmonics from 14).
2 : 7-*Dihydroxyanthracene* gives $\nu = 1065/26 \times 16/11 \times$ (harmonics from 41).
1 : 5-*Dihydroxyanthranol* gives $\nu = 1064\frac{1}{2}/27 \times 32/7 \times$ (harmonics from 13).
2-*Hydroxyanthraquinone* gives $\nu = 1065\frac{1}{2}/25 \times 25/13 \times$ (harmonics from 24).
2 : 6-*Dihydroxynaphthalene* gives $\nu = 1070/20 \times 5/2 \times$ (harmonics from 21).
1-*Hydroxyanthraquinone* gives $\nu = 1066\frac{1}{2}/25 \times 12/5 \times$ (harmonics from 19).

For comparison, Deslandres's results for simple compounds have been recalculated to the same basis, and the vulgar fractions come out quite simple and to some extent interconnected, namely, from $\frac{1}{12}$ to $\frac{1}{2}$.

The inference to be drawn from these considerations is that the absorptions of complex organic substances cannot be correlated with sub-atomic constants in the same way as the absorptions of simple substances.

The absorptions of complex and unsymmetrical substances, whilst no doubt *accompanied* by absorptions due to the valency electrons and the nuclei of the atoms, are therefore essentially molecular. These absorptions arise from the relative positions of the unsaturated atoms in the molecule (N, O, S, along with the group C : C), and will in course of time be fully and quantitatively explained either by Stieglitz's theory or my own.

Deslandres's theory and the harmonic part of the theory given in the British Association Report can be incorporated in mine by supposing that the constant 112 in my equation (connecting λ and molecular distance) is proportional to Deslandres's ratio $10^7 . r/1062\frac{1}{2}q$ (r = number of octets, q = harmonic number when the band is not the fundamental). Deslandres's quantity s is then no

longer a whole number or vulgar fraction, but is a function of a molecular distance of the form $a^{3/2}f(e)$, as given in Part I of this series (J., 1924, **125**, 1137).

GOVERNMENT LABORATORY,
JOHANNESBURG.

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CCXXXVIII.—*Some Observations on the Determination of Surface Tension by Means of Capillary Rise. The Surface Tension of Water, Ethyl Alcohol, Boron Trichloride, and Silicon Tetrachloride.*

By HERBERT MILLS and PERCY LUCOCK ROBINSON.

THE availability of sufficient quantities of boron trichloride and silicon tetrachloride of high purity, together with the absence from the literature of a determination of the surface tension of the former, and the doubtful nature of the value ascribed to the latter, prompted this investigation. To establish the necessary technique, work was begun on water, the value for which has been determined with sufficient frequency to warrant its use for this purpose. Ethyl alcohol was included because of the present uncertainty in the accepted surface tension of this liquid, and also in order to extend certain observations made in the course of the measurements with water.

The capillary-rise method for the determination of surface tension has received considerable attention in recent years, particularly by Richards and Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1656, where brief mention is made of previous work), Harkins and Brown (*ibid.*, 1919, **41**, 499), Richards and Carver (*ibid.*, 1921, **43**, 827), and Sugden (J., 1921, **119**, 1483). Study of the literature led at once to a decision to use the important suggestion of Sugden (*loc. cit.*) and Michaelis ("Praktik. d. physikal. Chemie," 1921, 61), *viz.*, that the difference in the capillary rise in two tubes should be used to measure surface tension. This constituted the most convenient method in that it removed at once the difficulty of ascertaining the exact height of the surface of the liquid in the containing vessel, which the elaborate experiments of Richards and Harkins (*loc. cit.*) and their co-workers were designed to overcome. In the present work, however, three instead of two capillary tubes were used, and a vacuum apparatus was devised capable of giving a good fall of liquid surface and of being completely submerged in a thermostat. All measurements were made in an atmosphere consisting solely of the vapour of the liquid in question.

Preliminary work showed that the level of the water in the capillaries fluctuated to an easily measurable extent over a very long period, and furthermore that the movements were not necessarily in the same direction in the three tubes at the same time. All the liquids examined behaved in this way.

Calculation of Surface Tension.

From the general formula relating surface tension to capillary rise, the equation

$$\gamma = r_1 r_2 g(3h + r_2 - r_1)(D - d)/6(r_1 - r_2)$$

may be derived, where r_1 and r_2 are the radii of two capillaries, h is the observed difference in height of two meniscuses in these tubes, D and d are, respectively, the densities of the liquid and the atmosphere over it, and g is the acceleration due to gravity. The value of g used was 981·45, and the surface tension, γ, is expressed in dynes per cm. In this investigation the capillaries were narrow enough to avoid any serious departure of the meniscuses from a hemispherical form, thus rendering unnecessary the corrections suggested by Sugden (*loc. cit.*). The diameters of tubes available were such that the rises in two were to nearly the same height, while that in the third was much lower, and as the proportional error in the measurements of h tends to increase as h diminishes, the smallest difference was not used in the calculation of surface tension.

EXPERIMENTAL.

The Preparation and Calibration of the Capillary Tubes.—The importance of a very rigorous cleaning of the capillary tubes cannot be overestimated: Harkins and Brown (*loc. cit.*), who gave this matter particular consideration, used prolonged passage of the vapour of the liquid concerned in the determination as the final cleaning process before use. The tubes here employed were steeped for several days in a solution of chromic acid in concentrated nitric acid, washed well by drawing water through them, almost submerged for 3 hours in boiling alcohol in such a manner that there was a continuous regular flow of liquid up through them, and finally steamed for 3 hours in the apparatus shown in Fig. 1—A is the capillary under treatment, B the jacket surrounding it, and C a tube of special form delivering steam under pressure from the purest distilled water. For the determinations with water the tubes were put into the apparatus wet from the steaming, but for the other determinations they were drained by holding them in a vertical position and touching the lower end with clean filter paper, and then dried at 110° in an electrically heated oven. After

their introduction into boiling alcohol the capillaries were handled only with several layers of clean filter paper between the fingers and the glass, in order entirely to prevent the possibility of the formation of a grease film.

The calibration of the capillary tubes was effected by three different methods in the case of A, B, and C, using (1) an ordinary physical travelling microscope, (2) a cathetometer, and (3) a travelling microscope, made by the Cambridge Instrument Company, and reading directly to 0·01 mm. and by estimation to 0·002 mm. The last instrument only was used in the case of D, E, and F. The mercury threads employed were weighed, after being removed from the tubes by means of dry air to a small glass weighing-bottle lid, on a special balance with calibrated weights, with the precautions usually taken in precise work. The weighings were to 0·01 mg. The uniformity of the bore was first examined by the introduction of a short thread of pure mercury, the length of which was accurately measured, in overlapping positions, along the whole length to be used. The results obtained by using the Cambridge instrument are in Table I, where the lengths of the threads are given in mm., and the figures marked with an asterisk denote the distance of the middle of the threads from the lower ends of the tubes.

FIG. 1.

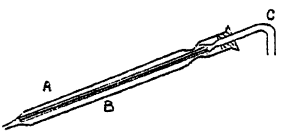


FIG. 2.

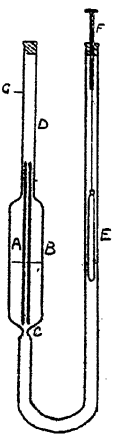


FIG. 3.

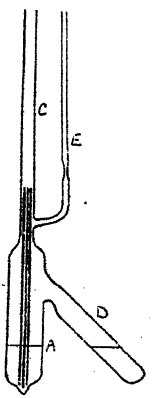


TABLE I.

A.		B.		C.	
8 cm.*	8·235	7 cm.*	10·980	8 cm.*	11·397
	8·246		10·991		11·391
	8·233	2 cm.*	10·991		11·395
	8·238				11·394
2 cm.*	8·247				11·399
				2 cm.*	11·396

D.		E.		F.	
8 cm.*	13·498	5 cm.*	14·757	4 cm.*	13·173
	13·478		14·767		13·174
	13·477		14·760	2 cm.*	13·164
2·5 cm.*	13·489	1 cm.*	14·757		

The uniformity of the tubes may be expressed as a maximum percentage difference in the length of the threads; the following results are obtained: A, 0·17%; B, 0·09%; C, 0·07%; D, 0·09%; E, 0·08%; F, 0·08%. These tubes compare unfavourably with those of Richards and Coombs (*loc. cit.*), for which uniformity was claimed, and also with those of Harkins and Brown (*loc. cit.*), where the difference was 0·03% on a thread of about 16·8 mm. in length, but they were the best from 50 lb. of capillary tubing, much of it specially drawn for this research, and their selection involved 4 weeks of constant work. The radii were obtained by measuring and weighing three threads about 4 cm. long and one or more shorter threads of pure mercury about 1 cm. long in each tube, the temperature at the time of measurement being noted and the density of the metal being computed (Smithsonian Physical Tables, 7th Edtn.). The observation of Harkins and Brown (*loc. cit.*) that there is a definite sag in the mercury meniscus with the tubes in a horizontal position even when the radius is as small as 0·2 mm. was confirmed; it was corrected for, as suggested by them, by subtracting the length and weights respectively of a shorter thread. The radii of the tubes were determined with the Cambridge measuring microscope, the calibrations being restricted to the lengths actually used, and are believed to have an accuracy of 0·1% and 0·05% for the narrower and the wider tubes respectively.

TABLE II.

Tube	A.	B.	C.	D.	E.	F.
r (in mm.)	0·07325	0·20168	0·25287	0·27165	0·41354	0·49920

The ends of all tubes were examined for ellipticity with a microscope and found to be satisfactory in this respect.

The Surface Tension of Water.—Preliminary work with three capillary tubes of approximately the bore indicated above showed that definite vertical movement of the meniscuses took place with the tubes either arranged in a triangular formation 4 cm. apart or bound together in a bundle. The results indicated that concordant surface tensions would be obtained from either arrangement provided that sufficient time was allowed to elapse after lowering the level of the liquid. This led to the construction of a vessel of the form indicated in Fig. 2, in which A represents the prepared capillaries, held in position in the wider tube, B, by the taper at C and the extension, D. The fall in level of the liquid was secured by raising the glass plunger, E, which was suspended from the long screw, F. This apparatus, charged with first-quality water, was submerged to the point G in a thermostat at 25° ± 0·01°, and the height of the water in the capillaries was observed by

means of a cathetometer reading to 0·01 mm. at intervals of about 10 minutes for 2·5 hours from the time at which the level of the liquid was lowered. During this period the heights of the menisci in the three tubes fell irregularly, giving, when plotted against time, a sinuous downward-sloping curve, recording maximum falls of 0·72 mm., 0·64 mm., and 0·74 mm., respectively. As the upper part of the apparatus, which was closed with a loosely fitting cork, had protruded from the bath, the fall was ascribed, correctly as it was subsequently proved, to evaporation. This explanation was tested by maintaining the bath at 17·4°, *i.e.*, about 0·5° below laboratory temperature, and repeating the observations without changing the water or re-treating the tubes; 24 observations, spread uniformly over 5 hours, were taken, with the result that sinuous, slightly rising curves were now obtained, showing minimum points 0·12, 0·17, and 0·17 mm., respectively, below the initial heights after about 2·5 hours, and a maximum rise at the end of the period of 0·39, 0·22, and 0·04 mm. above. Such changes could not be explained by either evaporation or irregular drainage, and further investigation was undertaken in an apparatus (Fig. 3) which consisted of a barrel, A, 2·5 cm. wide, terminated below in a cone-shaped point and above in the centrally disposed tube, C, suitable in width for holding steadily the three capillary tubes. The side limb, D, was provided for lowering the level of the liquid, and E with its capillary served for filling and evacuation. This vessel was cleaned with chromic–nitric acid mixture, well washed with distilled water, maintained full of boiling alcohol for 4 hours, and finally well rewashed with best-quality water. When thus prepared, the freshly steamed capillary tubes were slid down C into such a position that the three could be observed from the selected direction, and C was drawn off just above the tops of the capillaries. Water (prepared by treating first-quality distilled water with a trace of alkaline permanganate, redistilling with considerable rejection of head and tail fractions, and again twice distilling the main fraction with rejections) was used for the three final washes in the apparatus. These distillations were carried out successively without delay, and the final material, which was distilled directly into E, served as the sample to be examined. E was at once attached to the pump and the whole of the air was removed, the water being warmed to facilitate this, after which the apparatus was sealed off under the pressure of water vapour only. The surface-tension vessel was completely submerged in a thermostat maintained within $\pm$ 0·01° of the required temperature and, a fall in level of the liquid having been obtained by tilting the apparatus and allowing a portion to run into D, the heights

of the meniscuses were observed with a cathetometer reading to 0·01 mm. The tubes were arranged so that the threads of all could be observed without swinging the telescope of the instrument in a horizontal plane, both they and the cathetometer having been brought to a vertical position. The glass forming the barrel, A, had been carefully selected for uniformity and lack of distortion, and careful measurements, made at different places over the range actually used, indicated that the images of the meniscuses were not appreciably changed in apparent relative position. The regularity of the results derived from different sets of observations bears out this conclusion. Table III gives one complete set (Set K) of observations for water at 25° and indicates the general nature of the fluctuations in height observed throughout this work, namely, that the most rapid and extreme variations are found within the first hour, that these variations grow less with time, and that after a period of about 10 hours they have almost entirely vanished. Table IV gives the surface tension calculated from the data in Table III, and shows that the two values come closer together with the passage of time, the difference falling from 0·26 to 0·07 unit.

TABLE III.

Time from zero (min.) ...	6	18	34	50	86	123	158	219	271	340
Tube F (mm.)	0·62	0·77	0·71	0·69	0·72	0·75	0·75	0·78	0·78	0·78
Tube D (mm.)	25·56	25·41	25·49	25·46	25·48	25·49	25·52	25·53	25·56	25·55
Tube C (mm.)	29·59	29·60	29·63	29·65	29·60	29·62	29·67	29·66	29·66	29·71
Time from zero (min.) ...	389	458	520	575	636	696	754	787	813	
Tube F (mm.)	0·85	0·77	0·84	0·83	0·83	0·83	0·83	0·83	0·83	
Tube D (mm.)	25·55	25·56	25·58	25·60	25·63	25·64	25·64	25·64	25·64	
Tube C (mm.)	29·70	29·70	29·72	29·69	29·70	29·71	29·70	29·71	29·70	

TABLE IV.

	First hour.		Middle hour.		Last hour.	
Tubes.	Mean h (mm.).	γ.	Mean h (mm.).	γ.	Mean h (mm.).	γ.
C and F	28·920	72·31	28·900	72·26	28·875	72·20
D and F	24·783	72·05	24·770	72·01	24·810	72·13

TABLE V.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
I.	25°	11·5	C, F	28·86	72·16	72·16
J.	21	7	C, F	29·07	72·75	72·75
K.	25	14	C, F	28·88	72·20	72·17
			D, F	24·81	72·13	

Table V summarises the data for water using $(D - d)_{25°} = 0{\cdot}99705$ and $(D - d)_{21°} = 0{\cdot}99800$. In Sets I and J only one result is recorded because of the behaviour of tube E, which, although free from irregularity of bore or defect obvious under the microscope,

persisted in preventing water from rising beyond a certain point. Presumably this was due to some condition of the surface of the glass at this point which tended to inhibit wetting.

The Surface Tension of Alcohol.—A vessel similar to that described in the case of water was successively cleaned with chromic–nitric acid mixture, alkali, water, alcohol, and ether, and finally dried along with the capillary tubes, which had been treated as described previously, in an electrically heated oven. The alcohol used in Sets D and E was only roughly dried, that used in Set F was dried rather more thoroughly but still probably contained traces of moisture. Special precautions were, however, taken in the preparation of the alcohol for Set H, which was absolute alcohol redistilled with considerable rejections, refluxed over lime warm from burning for 3·5 days, the lime being changed at the end of the first day and a head and a tail fraction being rejected in the process. In distilling the liquid into the dried-out vessel, special precautions were taken to avoid contact with the air as far as possible; the whole operation lasted less than 0·25 hour and the apparatus was at once evacuated and sealed off. Table VI summarises the results for alcohol, all but Set H being considered as preliminary work with material containing water. The values $(D - d)_{25°} = 0{\cdot}78491$ and $(D - d)_{15°} = 0{\cdot}79352$ were used throughout.

TABLE VI.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.	Remarks.
C.	25°	4·0	A, B	49·81	22·04	22·06	Alcohol containing moisture.
			A, D	57·12	22·09		
E.	15	7·0	A, B	51·33	22·96	22·96	
			A, D	58·86	22·96		
F.	25	12	A, B	49·01	21·70	21·69	Drier alcohol.
			A, D	56·19	21·68		
H.	25	24	A, B	48·77	21·58	21·59	Dry alcohol.
			A, D	55·97	21·60		

The Surface Tension of Boron Trichloride.—Boron trichloride of high purity (for history of material and manipulation see subsequent paper by Parker and Robinson) was distilled into a similar surface-tension apparatus which had been thoroughly cleaned, dried, and evacuated. Two sets of observations were taken—at 25° with 15 readings, and at 21° with 10 readings. The data are given in Table VII, the values $(D - d)_{25°} = 1{\cdot}3144$ and $(D - d)_{21°} = 1{\cdot}3207$ being used.

The Surface Tension of Silicon Tetrachloride.—The procedure was exactly as with boron trichloride (for history of material and manipulation see Parker and Robinson, *loc. cit.*), but, unfortunately,

TABLE VII.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
M.	25°	10	A, B	21·71	16·07	16·07
			A, D	24·91	16·07	
N.	21	9·5	A, B	22·22	16·52	16·52
			A, D	25·49	16·52	

at the end of the distillations the sudden boiling of a drop or two of liquid in the plunger arm of the special joint caused a fracture, and air entered the apparatus. The broken portion was at once drawn off and the apparatus attached to the pump and evacuated so that exposure to air was not longer than 1·5 minutes. There was no evidence of hydrolysis in the apparatus, nor did the behaviour of the liquids in the capillaries suggest that the admission of air had had any detrimental effect; nevertheless, these results are given provisionally and it is proposed to repeat this portion of the work with other material of similar purity which is available. Table VIII gives these provisional results, 15 observations being taken in each set; $(D - d)_{25°} = 1{\cdot}4685$ and $(D - d)_{21°} = 1{\cdot}4771$ were used.

TABLE VIII.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
O.	25°	12	A, B	23·11	19·11	19·11
			A, D	26·51	19·11	
P.	21	12	A, B	23·54	19·58	19·59
			A, D	27·01	19·59	

Discussion.

It has been shown that tubes of a much smaller bore than have usually been employed can be used in the determination of surface tension to a high degree of accuracy by the method suggested by Sugden (*loc. cit.*), but concordant results with two or more such tubes are obtained only several hours after the lowering of the liquid level. The thorough cleaning of the capillaries emphasised by other workers is found to be necessary. Distinct advantage attends the use of three in place of two tubes, and the results are the same whether they be separated from one another by several cm. or bound together in a bundle, the latter arrangement being more convenient. During the first hour or so, the meniscuses in the capillary tubes show slow oscillations, sometimes opposite in direction in two tubes at the same time, or coinciding with no movement in another tube, while the mean heights tend to decrease throughout the same period, and surface tensions calculated from differences in the heights obtained at any moment do not show

good agreement amongst themselves. These movements gradually decrease and are followed by a series of more or less spasmodic rises which continue, although they may be separated by intervals as long as one or two hours, until the maximum rise for each tube is reached. That these rises are to be ascribed to surface forces, and not to any change in level of the main liquid surface from drainage or other causes, is proved by the fact that they are invariably preceded by a greatly increased curvature of the meniscus, as though the centre were being drawn down, whilst, furthermore, the movements take place at times and to extents which are not the same in the different tubes.

If the forces producing the rises were being applied at the base of the columns, a flattening of the meniscuses and concurrent rises in the three tubes would be anticipated. The whole subject is being investigated, but a careful examination of the available data leads to the conclusion that for the same liquids the changes in the heights of the meniscuses decrease with increasing size of capillary, while the period required to reach the maximum rise and the equilibrium is slightly less in the wider tubes, and that with the same bore the magnitude of these changes in the liquids considered grows less in the order alcohol, water, silicon tetrachloride, boron trichloride. The inference made here is that, after the oscillations of the initial period have damped down, the change in level of the meniscus due to spasmodic rises is probably related to viscosity, for the viscosities of alcohol and water are known to decrease in the order noted, while those of the chlorides, although apparently not determined, are certainly less than that of water. It is suggested that the maximum rise attained when the meniscuses are at rest corresponds to the true static equilibrium between surface energy and gravity, and that the figure calculated from h in these conditions corresponds to the true surface tension. It should be pointed out that, once equilibrium is reached, the meniscuses are not observed to move either of their own accord or when the vessel has been made to tremble by tapping, thus suggesting the stability above implied.

Surface tensions are usually given at 20°, and Table IX records the values now found (in contact with only the vapour of the substance) corrected to this temperature, together with the change per degree.

TABLE IX.

Substance.	γ.	Change in γ per degree.
Water	72·90 ± 0·04	0·15
Alcohol	22·05 ± 0·01	0·09
Boron trichloride	16·70 ± 0·01	0·11
Silicon tetrachloride	19·71 ± 0·01	0·12

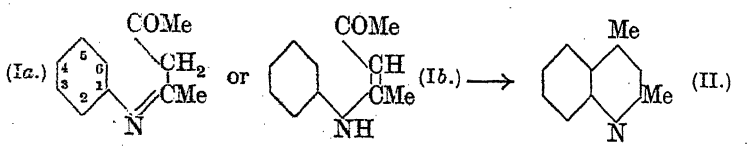
The value for water agrees most closely with the 72·80 of Harkins and Brown (*loc. cit.*), but is much higher than the 72·74 of Richards and Coombs (*loc. cit.*), the 72·70 of Sugden (*loc. cit.*), the 72·61 of Worley (J., 1914, **105**, 266), or the 72·8 given as the most probable value by Freundlich ("Colloid and Capillary Chemistry," 1927, 24). In the case of alcohol there have been numerous previous determinations yielding results varying from 21·2 to 22·4. The value given above agrees closely with the 22·0 of Ramsay and Shields (*Phil. Trans.*, 1893, **184**, 647), and the precautions taken in this work render it the most probable value at the present time. The surface tension of boron trichloride has not hitherto been recorded. Silicon tetrachloride has received attention from Ramsay and Shields (*loc. cit.*), who found $\gamma = 16{\cdot}31$ at 18·9°, *i.e.*, 16·20 at 20°; from Walden (*Z. anorg. Chem.*, 1900, **25**, 218), who found $\gamma = 18{\cdot}20\ (1 - 0{\cdot}00548t)$, *i.e.*, 16·23 at 20°; and from Mendeléev (*Pogg. Ann.*, 1870, **141**, 618), who found 15·13 at the b. p. (57°), which is approximately equivalent to 19·20 at 20°.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, May 9th*, 1927.]

CCXXXIX.—*The Factors controlling the Formation of Some Derivatives of Quinoline, and a New Aspect of the Problem of Substitution in the Quinoline Series.*

By ELWYN ROBERTS and EUSTACE EBENEZER TURNER.

AN apparently excellent method for obtaining quinoline derivatives (II) is that devised by Combes (*Bull. Soc. chim.*, 1888, **49**, 90; *Compt. rend.*, 1887, **106**, 142), namely that of warming, with concentrated sulphuric acid, the condensation products (I*a* or I*b*) of acetylacetone with primary aromatic amines:



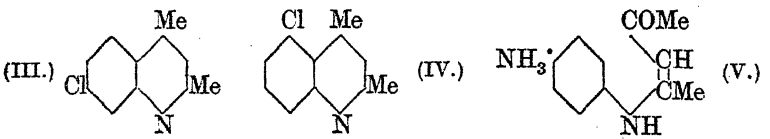
Previous work has shown that most simple substituted anilines condense readily with acetylacetone, even where, as in 2 : 6-dimethoxyaniline, a marked steric effect must be supposed to occur (Turner, J., 1917, **111**, 1), and it has now been found that, although *o*-, *m*-, and *p*-chloro-, 2 : 4-, 3 : 4-, and 3 : 5-dichloro-aniline do so, 2 : 5-dichloroaniline condenses only partially. The case of condens-

ation appears to be affected most by the basicity of the aniline used, for no nitroaniline, simple or complex, can be caused to condense with acetylacetone. It may be noted that acetylacetone condenses less well with most bases than does, for example, salicylaldehyde, which rapidly converts 2 : 5-dichloroaniline into the o-*hydroxybenzylidene* derivative.

The second stage of the Combes quinoline synthesis, namely, the intramolecular condensation of an anil of acetylacetone, is, however, much more definitely affected by the nature of the substituents present. Thus, whilst the condensation products, with acetylacetone, of aniline and *p*-toluidine (Combes, *loc. cit.*), those of 2 : 3-, 2 : 5-, and 3 : 4-dimethoxyaniline, that of 2-bromo-4 : 5-dimethoxyaniline (Lions, Perkin, and Robinson, J., 1925, **127**, 1158), and, as now shown, that of *m*-chloroaniline readily pass into the corresponding substituted 2 : 4-dimethylquinolines, a number of not very dissimilar anils do not, under corresponding conditions, undergo conversion into quinolines to any measurable extent. Into this second class fall the condensation *products*, with acetylacetone, now examined for the first time, of *o*- and *p*-chloroanilines, 2 : 4-, 2 : 5-, and 3 : 5-dichloroanilines, and *o*-anisidine. Koenigs and Mengel (*Ber.*, 1904, **37**, 1322) were similarly unable to obtain 6-methoxy-2 : 4-dimethylquinoline from β-*p*-methoxyanilinopropenyl methyl ketone. Marckwald and Schmidt (*Annalen*, 1893, **274**, 331) showed that, whilst both *m*- and *p*-phenylenediamines condensed with two molecules of acetylacetone, treatment of the products with concentrated sulphuric acid afforded an amino-2 : 4-dimethylquinoline (and not a phenanthroline) in the former case, and no quinoline at all in the second. Incidentally, Bülow and Issler (*Ber.*, 1903, **36**, 4013) effected the conversion of β-*m*-hydroxyanilinopropenyl methyl ketone into a mixture of hydroxy-2 : 4-dimethylquinolines by using, not concentrated sulphuric acid, but hydrogen chloride and glacial acetic acid as the condensing medium.

It appears possible to draw certain definite conclusions from these facts. For example, when a strongly ortho-para directing group is present in the meta-position to the nitrogen atom [3 or 5 in (I)], condensation proceeds readily, even if a similar group is present in an unfavourable position, as in 2 : 5-, 3 : 4-, and 2 : 3-dimethoxyaniline. On the other hand, a strongly ortho-para directing group present in position 4 (I), in absence of other substituents in favourable positions, appears to be sufficient to prevent quinoline formation (*o*- and *p*-anisidine). The effect of chlorine is what would be anticipated from our knowledge of its power as a directive influence. Thus, whilst one chlorine atom in a favourable

position (meta to the nitrogen atom) is associated with exceptional ease of quinoline formation, a chlorine atom in another position prevents condensation (but compare the case of 3 : 4-dichloroaniline, below). It therefore seems that in these cases the ortho-directive influence of the nitrogen atom is, extraordinary though it may appear, feebler than the opposing ortho-para influence of a chlorine atom. Further, whilst steric factors do not prevent the operation of the directive influence of a methoxyl group, they appear to more than neutralise that of even two chlorine atoms. Thus, β-3 : 5-dichloroanilinopropenyl methyl ketone [chlorine in positions 3 and 5 in (I)] cannot be converted into the corresponding quinoline, although the two chlorine atoms and the nitrogen atom would be expected to favour condensation. From this fact, one might deduce that the dimethylquinoline formed from *m*-chloroaniline would be (III) rather than (IV), since the steric effect would operate against the formation of the latter. That this inference is correct is proved

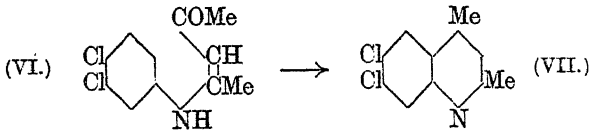


later. It would also appear to follow from this that the compound obtained by Marckwald and Schmidt (*loc. cit.*) from *m*-phenylenediamine is 7-amino-2 : 4-dimethylquinoline. The non-formation of a quinoline from *p*-phenylenediamine is of interest, for, since β-*p*-aminoanilinopropenyl methyl ketone is presumably present as the ion (V) in concentrated sulphuric acid solution, the most favoured position would appear to be that where condensation could occur, but does not.

It is somewhat difficult, on the other hand, to explain why β-*p*-toluidinopropenyl methyl ketone [methyl in position 4 in (I)] is quantitatively converted into 2 : 4 : 6-trimethylquinoline (see Experimental). For, since *p*-chlorotoluene nitrates to roughly equal extents in the 2- and 3-positions (Holleman, *Rec. trav. chim.*, 1909, **28**, 408), the influence of a methyl group should approximate to that of a chlorine atom in type (I). The explanation may be, however, that just as replacement by chlorine, but not by methyl, diminishes the basicity of the aniline molecule, so it diminishes the ortho-para directive influence, already small, of the nitrogen atom in the acetylacetone anils.

Particular interest attaches to the action of sulphuric acid upon the condensation product of acetylacetone with 3 : 4-dichloroaniline (VI). Preliminary experiments showed no condensation, but then, on one occasion, a good conversion into a dichlorodimethylquinoline,

m. p. 119—120°, occurred. Attempted repetition of the successful experiment on at least a dozen occasions never gave an isolable quantity of this product, which, however, has been shown to be 6 : 7-*dichloro*-2 : 4-*dimethylquinoline* (VII).



We regard these results as indicating that in (VI) there is a very delicate balance between the antagonistic and the favourable influences, so that the slightest variation from the ideal conditions for condensation is sufficient to prevent ring closure.

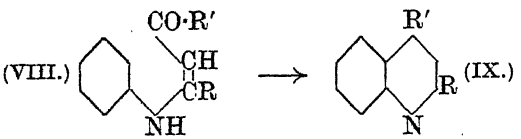
The non-formation of quinoline in the cases referred to above can hardly be due to an initial condensation to the extent of a few units %, the water formed then, with the sulphuric acid, hydrolysing the unchanged anil of a weak base, for if this were so, condensation should have been observed where absolute or slightly fuming sulphuric acid was used.

Partly in order to prove the constitution of the products (III) and (VII), and partly to institute a comparison of the Combes condensation with others leading to the same, and other, quinolines, we next directed our attention to the method first used by Reed (*J. pr. Chem.*, 1885, **32**, 630), but generally known as the Beyer condensation (*ibid.*, 1886, **33**, 393). When heated with a suitably aged mixture of paraldehyde, acetone, and hydrogen chloride at 100° in presence of nitrobenzene, *o*-, *m*-, and *p*-chloro-, 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-dichloro-, and 2 : 4 : 5-trichloro-aniline were converted into dimethylquinolines, although in every case the yield was poor. On the other hand, *m*-nitroaniline was apparently unaffected, whilst *o*-nitroaniline was converted in good yield into a *compound* other than the expected 8-nitro-2 : 4-dimethylquinoline. Again, 3-chloro-6-nitro- and 3 : 4-dichloro-6-nitro-aniline were converted into tarry substances from which nothing could be isolated. The object of attempting the latter two condensations was to synthesise reference compounds needed for the elucidation of the structure of (III) and (VII).

When on one occasion 3 : 5-dichloroaniline was heated with a paraldehyde–acetone–hydrogen chloride mixture prepared 2 months previously, no 5 : 7-dichloro-2 : 4-dimethylquinoline was obtained, but, in good yield, a *substance* which has not yet been identified.

The above results become of even greater interest when the Combes and the Beyer condensation are compared with those of Doebner and von Miller and of Skraup. The last three of these

condensations have been the subject of repeated investigation, but much uncertainty still exists as to the precise mechanism underlying them. Consideration of the papers of von Miller (*Ber.*, 1891, **24**, 1720; 1892, **25**, 2072), Jones and his collaborators (J., 1910, **97**, 632; 1911, **99**, 334; 1912, **101**, 1376), Blaise and Maire (*Compt. rend.*, 1907, **144**, 93; *Bull. Soc. chim.*, 1908, **3**, 658), and Simon (*Compt. rend.*, 1907, **144**, 138) suggests, however, that the four reactions under discussion are similar in one respect, namely, that in the last stage they all appear to conform to the general scheme of (VIII) passing into (IX):



The Skraup, Doebner–Miller, Beyer, and Combes condensations are represented by this scheme when R = R′ = H, R = Me and R′ = H, R = R′ = Me, and R = R′ = Me, respectively. The assumption is not invalidated by the observations of Knoevenagel and his collaborators (*Ber.*, 1922, **55**, 1923; 1923, **56**, 2414), nor can the fact that the so-called "aldol bases" are formed in the Doebner–Miller reaction be regarded as involving a conception essentially different from that represented by the above scheme.

Decker and Remfry (*Ber.*, 1905, **38**, 2773) concluded that both the Skraup and the Doebner–Miller reaction converted mono-meta-substituted anilines into 5-substituted quinolines. A closer examination of the facts, however, shows that this is hardly the case, since Skraup reactions with these compounds actually fall into two classes. Those in which the meta-substituent is meta-directing (NO_2, SO_3H, and CO_2H) give almost entirely 5-substituted quinolines (La Coste, *Ber.*, 1883, **16**, 669; Claus and Stiebel, *Ber.*, 1887, **20**, 3095; Knueppel, *Ber.*, 1896, **29**, 703; Decker, *J. pr. Chem.*, 1901, **63**, 573; **64**, 85; Lellmann and Lange, *Ber.*, 1887, **20**, 1446; Schlossen and Skraup, *Monatsh.*, 1881, **2**, 518; Skraup, *Ber.*, 1882, **15**, 893; Skraup and Bronner, *Monatsh.*, 1886, **7**, 139, 519; Lellmann and Alt, *Annalen*, 1887, **237**, 307), whilst, when the meta-substituent is ortho-para directing (Cl, Br, Me, OH), either a mixture of 5- and 7-derivatives results, or almost exclusively the 7-derivative (La Coste and Bodewig, *Ber.*, 1884, **17**, 926; La Coste, *Ber.*, 1885, **18**, 2940; Claus and Tornier, *Ber.*, 1887, **20**, 2872; Claus and Vis, *J. pr. Chem.*, 1889, **40**, 382; Skraup, *Monatsh.*, 1882, **3**, 381, 531; Skraup, *loc. cit.*; Skraup and Bronner, *loc. cit.*; von Braun, Gmelin, and Schultheiss, *Ber.*, 1923, **56**, 1341). On the other hand, *m*-

nitroaniline gives mainly 5-nitroquinaldine (Decker and Remfry, *loc. cit.*), whilst it does not condense to any observable extent under the conditions of the Beyer synthesis.

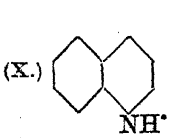
m-Chloroaniline gives rise to a mixture of 5- and 7-derivatives in the Skraup reaction (La Coste, 1885, *loc. cit.*; Claus and co-workers, *J. pr. Chem.*, 1893, **48**, 253, 270), mainly to the 7-derivative in the Beyer reaction, and to the 7-derivative only in the Combes condensation. An inspection of (VIII) and (IX) suggests that the difference in position of condensation in the three reactions mentioned is due to the steric effect of R′. Possibly the same effect prevents the formation of 5-nitro-2 : 4-dimethylquinoline by the Beyer process, since for some reason, not clear at present, the quinoline ring apparently prefers to form in the ortho-position with respect to a nitro-group rather than in the para-position. This point is of considerable interest, since in the nitration of nitrobenzene, more ortho- than para-substitution occurs.

Which constitution (I*a* or I*b*) more accurately represents the constitution of the condensation products of acetylacetone with anilines cannot now be discussed, but we have observed that dibenzoylmethane condenses with freshly distilled aniline to give, as one product, a compound identical with that obtained by Watson (J., 1903, **83**, 1326) by the addition of aniline to benzoylphenylacetylene, CPh:C·COPh. Watson regarded his compound as being either CHPh:C(NHPh)·COPh or NHPh·CPh:CH·COPh, and the formation of the same compound from dibenzoylmethane shows that the latter reacts in the enolic form, to give the second of the two substances formulated, *i.e.*, to give the anilino-derivative and not the phenylimino-compound, COPh·CH_2·CPh:NPh. One of us has previously observed (Turner, *loc. cit.*) that when acetylacetone is heated with excess of aniline it undergoes scission, giving acetanilide. We have now found that benzanilide is formed as a second product when aniline reacts with dibenzoylmethane.

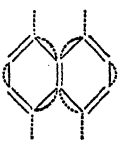
The factors governing substitution in quinoline compounds are apparently less complex than would be assumed from first considerations. Quinoline and 2-methylquinoline both nitrate simultaneously in the 5- and 8-positions (Claus and Kramer, *Ber.*, 1885, **18**, 1243, etc.), whilst 4-methylquinoline, on the other hand (Busch and Königs, *Ber.*, 1890, **23**, 2687), gives only the 8-nitro-derivative, an effect almost certainly due to the steric influence of the methyl group in position 4. 2 : 4-Dimethylquinoline would therefore also be expected to nitrate in position 8, and has actually been found to do so. The *nitro*-compound on reduction gives 8-*amino*-2 : 4-*dimethylquinoline*, and the latter is converted by the Gattermann diazo-method into 8-*chloro*-2 : 4-*dimethylquinoline*,

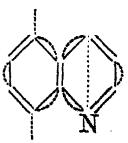
identical with the product of the Beyer condensation, using *o*-chloroaniline.

It would be thought that most of the substitution reactions of quinoline could be referred to the presence of the nitrogen atom, but actually this is not the case. Nor is it quite clear by what process conditions of nitration affect the proportion of 5- and 8-substitution in quinoline itself. For example, when quinoline nitrate is added to fuming sulphuric acid, 5-nitroquinoline results (Dufton, J., 1892, **61**, 783), whilst mixed acid converts quinoline itself mainly into the 8-isomeride (Kŏnigs, *Ber.*, 1879, **12**, 449). If the former nitration were explained as that of the ion (X), and the latter as that of the free base, then it would be difficult to explain why *iso*-



(X.)


(XI.)

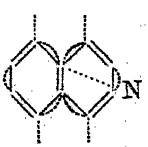


(XII.)

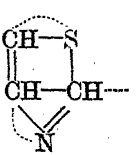
quinoline does not nitrate in position 7 (Claus and Hoffmann, *J. pr. Chem.*, 1893, **47**, 253), and even more so why quinolinium methonitrate also nitrates in positions 5 and 8 (Decker, *Ber.*, 1905, **38**, 1274). A comparison of quinoline and naphthalene appears to solve these difficulties, for, just as the behaviour of naphthalene is tolerably well explained by Thiele's formula (XI), so that of quinoline should be explained, at least to a considerable extent, by (XII), the following two facts being borne in mind: (1) Mills and Smith (J., 1922, **121**, 2724) concluded that in the naphthalene molecule the two central (*i.e.*, un-numbered) carbon atoms are joined by a double bond, (2) the pyridine molecule is markedly non-reactive, a property capable of explanation by formulating it as (XIII), since the highly unsaturated nitrogen atom may be assumed to take up residual affinity from the 4-position. That is, one would expect to find reactivity in the 5- and 8-positions in quinoline, corresponding to the reactivity of the *four* α-positions in naphthalene.



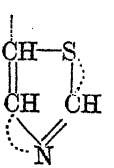
(XIII.)



(XIV.)



(XV.)



(XVI.)

Indeed, the application of similar reasoning to the *iso*quinoline and thiazole molecules suggests an alternative explanation of the interesting results obtained by Mills and Smith (*loc. cit.*), *viz.*, in

*iso*quinoline, chlorine * should be more reactive (towards hydriodic acid and red phosphorus) in position 1 than in position 3, and in thiazole, since the nitrogen atom is less saturated than the sulphur atom (compare XV and XVI), reactivity should be associated more with position 2 than with position 4—which is actually the case. If this explanation is correct, reactivity should also be greater in position 5 than in position 4.

If (XIV) accurately represents the *iso*quinoline molecule, the known nitro-derivative might be expected to be the 5- rather than the 8-compound.

Quinoline actually resembles naphthalene very strongly in its substitution reactions, since α-nitronaphthalene corresponds with either 5- or 8-nitroquinoline. The analogy becomes even more striking when it is realised that, just as naphthalene-α-sulphonic acid is converted by concentrated sulphuric acid under definite conditions into the β-isomeride, so quinoline-5-sulphonic acid is converted by the same reagent at 250—300° into the 6-isomeride (Lellmann and Reusch, *Ber.*, 1889, **22**, 1391).

Nitration of 6-, 7-, and 8-chloro-2 : 4-dimethylquinoline appears to be controlled almost entirely by 5 : 8 reactivity, and by the ortho-para directive influence of the chlorine atom, which can act partly in the same sense. These overcome the steric effects which must be assumed in the case of the 6- and the 7-chloro-compound [compare the nitration, by Armstrong and Wynne, of β-chloronaphthalene, where the α-position *could* be avoided, and is (*Chem. News*, 1889, **59**, 225)]. For example, 6-chloro- and 7-chloro-2 : 4-dimethylquinoline nitrate in positions 5 and 8, respectively. The 8-chloro-compound nitrates in position 5, as is shown by the fact that the *nitro*-compound, on reduction, affords an *amino*-compound which is convertible into 5 : 8-*dichloro*-2 : 4-*dimethylquinoline*, identical with the product of Beyer condensation on 2 : 5-dichloroaniline.

That the ortho-para directive influence of the chlorine atoms in these compounds operates is shown by the results of nitrating 6- and 7-chloro-2 : 4-dimethylquinoline. The effect of 5 : 8-reactivity in the quinoline series is shown very clearly by the fact that 6-bromoquinoline sulphonates in position 8 (Edinger, *Ber.*, 1908, **41**, 937), whilst 6-chloroquinoline sulphonates either in 5 or in 8, according to conditions (Claus and Schedler, *J. pr. Chem.*, 1894, **49**, 355). An even more striking case is that recorded by Kaufmann and Hussy (*Ber.*, 1908, **41**, 1735), who showed that 6- and 7-nitroquinoline nitrate to give, respectively, 5 : 6- and 6 : 8-, and 5 : 7- and 7 : 8-

* The chlorine atom here appears to be of the positive type.

dinitroquinoline, *i.e.*, 5 : 8-reactivity causes some nitration to occur in the ortho-position to a nitro-group.

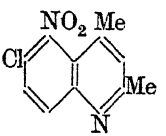
Dichloro-derivatives of 2 : 4-dimethylquinoline also nitrate quantitatively to give only one product. Thus the 5 : 8-dichloro-derivative gives 5 : 8-*dichloro*-6-*nitro*-2 : 4-*dimethylquinoline*, whose constitution is proved by its conversion, through the corresponding 6-*amino*-compound, into 5 : 6 : 8-*trichloro*-2 : 4-*dimethylquinoline*, also obtained by Beyer condensation of 2 : 4 : 5-trichloroaniline. Nitration of other dichloro-compounds undoubtedly occurs in position 5 or 8, but it has been impossible to prove the constitutions of the products, since the amines obtained by reduction could not be converted into the corresponding chloro-compounds. We have confirmed the observation made by Claus (compare *J. pr. Chem.*, 1894, **49**, 355) that the Sandmeyer reaction is unsuitable in the quinoline series, whereas the Gattermann method gives good results. On the other hand, the success of a replacement of an amino-group by chlorine depends also on the basicity of the amino-compound, and on the rate of diazotisation of the hydrochloride; for example, whilst 8-amino-, 6-*chloro*-5-*amino*-, 8-chloro-5-amino-, and 7-*chloro*-8-*amino*-2 : 4-*dimethylquinoline* diazotise readily, 5 : 8-dichloro-6-amino-2 : 4-dimethylquinoline diazotises slowly, 6 : 8-*dichloro*-5(?)-*amino*- still more slowly, and 5 : 6-*dichloro*-8(?)-*amino*- hardly at all. 5 : 6 : 8-Trichloro-2 : 4-dimethylquinoline does not undergo nitration under the conditions employed.

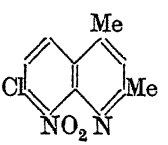
It was stated above that 3 : 4-dichloroaniline was converted by the Combes reaction into 6 : 7-dichloro-2 : 4-dimethylquinoline, but this fact was only established with considerable difficulty. *o*-Dichlorobenzene was found to condense readily with acetyl chloride under Friedel–Crafts conditions to give 3 : 4-*dichloroacetophenone*, but the nitration of the latter caused unexpected difficulties. These were finally overcome, and the 3 : 4-*dichloro*-2-*nitroacetophenone* obtained was converted into the corresponding *amino*-compound, which, when heated with acetone and a trace of alkali, gave an almost quantitative yield of 6 : 7-dichloro-2 : 4-dimethylquinoline, m. p. 119—120°, identical with the product from 3 : 4-dichloroaniline. The proof of the constitution of this product enabled us to deduce the constitution of the product of nitration of 6-chloro-2 : 4-dimethylquinoline. When this was reduced and the resulting amine was submitted to the Gattermann reaction, a dichlorodimethylquinoline was obtained, also melting at 119—120°; this depressed the m. p. of the synthetic 6 : 7-isomeride, and was therefore 5 : 6-dichloro-2 : 4-dimethylquinoline, since the 6 : 8-isomeride, obtained by Beyer condensation of 2 : 4-dichloroaniline, melted at 148—148·5°.

The chloro-2 : 4-dimethylquinoline obtained by the Combes reaction from *m*-chloroaniline, and therefore either the 5- or the 7-derivative, gave a nitro-compound which was converted into a chloroamino-compound, and thence into a dichloro-compound melting at 104—104·5°. The latter could only be 5 : 6-, 5 : 7-, 5 : 8-, 6 : 7-, or 7 : 8-dichloro-2 : 4-dimethylquinoline. Of these compounds, three were already known, and 5 : 7-*dichloro*-2 : 4-*dimethylquinoline*, obtained by Beyer condensation from 3 : 5-dichloroaniline, was found to melt at 84—86°. It therefore follows that the above chlorodimethylquinoline is the 7-derivative, and the derived dichlorodimethylquinoline the 7 : 8-derivative.

6-*Chloro*-5-*nitro*-2 : 4-*dimethylquinoline* was found not to react with piperidine, and this led us to consider again the work of Mills and Smith (*loc. cit.*). If, with these authors, we assume the presence of a central double bond in the quinoline molecule, the 6-chlorine atom and the 5-nitro-group will be attached to carbon atoms joined by a double bond (XVII), a condition assumed by Borsche and his co-workers (*Annalen*, 1913, **402**, 81; 1926, **447**, 1) to be associated with diminished reactivity of chlorine. One of these assumptions—we think that due to Borsche—appears to be incorrect, since 7-*chloro*-8-*nitro*-2 : 4-*dimethylquinoline* (XVIII), in which almost similar conditions obtain, reacts readily with piperidine to give 8-*nitro*-7-*piperidino*-2 : 4-*dimethylquinoline*.

(XVII.)





(XVIII.)

We have also investigated the chlorination of various chloro-derivatives of 2 : 4-dimethylquinoline in presence of glacial acetic acid and anhydrous sodium acetate. 7-Chloro-2 : 4-dimethylquinoline gave a *trichloro*-derivative, whilst 6- and 8-chloro- and 5 : 6-dichloro-2 : 4-dimethylquinoline gave *tetrachloro*-2 : 4-*dimethylquinolines*, all different. 5 : 8-Dichloro-2 : 4-dimethylquinoline, however, gave a *pentachloro*-2 : 4-*dimethylquinoline*, identical with the product of chlorinating the 6 : 8-compound. All these compounds contain mobile chlorine (of the negative type), showing that chlorination has occurred partly in the methyl groups. Similar compounds were obtained by Kŏnigs from 8-nitro-4-methylquinoline (*Ber.*, 1898, **31**, 2368) and later by Hammick (J., 1923, **123**, 2882). Little can be said with regard to the constitutions of our compounds, except that the pentachloro-compound must, because of its dual origin, contain chlorine atoms in the 5-, 6-, and 8-positions. The

extent to which chlorination occurs is apparently determined neither by the amount of sodium acetate used, nor by the solubility of the compounds actually isolated.

EXPERIMENTAL.

Condensation of Substituted Anilines with Acetylacetone.—The general method adopted was to allow a mixture of the substituted aniline (1 mol.) with 1·1 mols. of acetylacetone to boil gently under reflux for 1—2 hours. The cooled product was then thoroughly shaken with water, benzene added, and the two layers separated. The benzene solution was shaken twice or thrice with water, dried over anhydrous sodium sulphate, and heated at 100° until free from benzene. In most cases, the anil was then pure enough to solidify when cooled.

p-Toluidine.—The anil was obtained in almost theoretical yield, and after one crystallisation from light petroleum (b. p. 40—60°) formed massive prisms, m. p. 68—69°. Combes (*loc. cit.*) gave m. p. 39—40°, whereas in D.R.-PP. 363,582 and 363,583 the m. p. is given as 65·5°. Ferriss and Turner (J., 1920, **117**, 1140) stated that the anil was converted, under the conditions now given for its formation, into 2 : 4 : 6-trimethylquinoline. This, however, is not the case. The anil, β-*p*-toluidinopropenyl methyl ketone, when treated with sulphuric acid by the usual method (see below) was quantitatively converted into 2 : 4 : 6-trimethylquinoline, m. p. 43—45°. The m. p. (63—64°) quoted by Pfitzinger (*J. pr. Chem.*, 1888, **38**, 40) is evidently that of the hydrate, which we have found to melt at 63—65°. The concentrated sulphuric acid solution of the crude quinoline, when treated with potassium dichromate, remained a clear reddish-brown colour after some minutes' boiling, indicating the absence of even small quantities of *p*-toluidine. Such quantitative conversion into a quinoline was not observed with the product from any other substituted aniline.

o-*Chloroaniline.*—β-o-*Chloroanilinopropenyl methyl ketone* was readily formed, and separated from light petroleum (b. p. 40—60°) in small plates, m. p. 66—67° (Found: Cl, 17·1. $C_{11}H_{12}ONCl$ requires Cl, 16·9%).

p-*Chloroaniline.*—β-p-*Chloroanilinopropenyl methyl ketone* was readily obtained, and crystallised from light petroleum (b. p. 40—60°) in rectangular prisms, m. p. 60—61° (Found: Cl, 17·0%).

m-*Chloroaniline.*—β-m-*Chloroanilinopropenyl methyl ketone*, readily formed, crystallised from light petroleum (b. p. 40—60°) in plates; it had m. p. 42°, and b. p. 187°/13 mm. (Found: N, 6·9. $C_{11}H_{12}ONCl$ requires N, 6·7%).

o-*Hydroxybenzylidene*-3-*chloroaniline* was readily obtained, and separated from alcohol in bright yellow needles, m. p. 99° (Found: N, 6·1. $C_{13}H_{10}ONCl$ requires N, 6·0%).

2 : 4-*Dichloroaniline*.—This base condensed readily with acetylacetone. β-2 : 4-*Dichloroanilinopropenyl methyl ketone* separated from aqueous alcohol in needles, m. p. 100·5° (Found: N, 5·8. $C_{11}H_{11}ONCl_2$ requires N, 5·7%). o-*Hydroxybenzylidene*-2 : 4-*dichloroaniline* separated from alcohol in brilliant yellow needles, m. p. 90·5° (Found: N, 5·3. $C_{13}H_9ONCl_2$ requires N, 5·3%).

2 : 5-*Dichloroaniline*.—The condensation of this base with acetylacetone presents two interesting features. When any other of the substituted anilines dealt with was heated with acetylacetone at 100° (the approximate b. p. of such mixtures), water was seen to separate after a few minutes. In the case of 2 : 5-dichloroaniline, however, water only separated from the condensation mixture when the latter was boiling briskly. On cooling it a few degrees, the water redissolved. The second peculiarity observed was the small yield obtained, so that the β-2 : 5-*dichloroanilinopropenyl methyl ketone* was only isolable by distillation under diminished pressure (b. p. 190—200°/15 mm.) of the purified reaction product. It finally crystallised from light petroleum (b. p. 40—60°) in octahedra, m. p. 46°. o-Hydroxybenzylidene-2 : 5-dichloroaniline, on the other hand, was readily obtainable in good yield; the crude product crystallised from alcohol in bright yellow needles, m. p. 107° (Found: N, 5·4%).

3 : 5-*Dichloroaniline*.—Condensation occurred readily, but the β-3 : 5-*dichloroanilinopropenyl methyl ketone* was not obtained crystalline. The 3 : 5-dichloroaniline required was obtained by reducing 3 : 5-dichloronitrobenzene by the iron method, the nitro-compound being prepared as follows (compare Holleman and Reiding, *Rec. trav. chim.*, 1904, **23**, 366): A mixture of 85 g. of 2 : 6-dichloro-4-nitroaniline and 170 c.c. of concentrated sulphuric acid was diazotised at −5° with 56 g. of solid sodium nitrite. The dark paste obtained was slowly run into 600 c.c. of boiling 96% alcohol; immediate decomposition then took place, with the formation of an orange solution. Some sodium sulphate separated, and on diluting the mixture largely with water, the nitro-compound was precipitated. It had m. p. 62—65°, whereas the pure substance melts at 65°.

3 : 4-*Dichloroaniline*.—This base condensed smoothly with acetylacetone to give β-3 : 4-*dichloroanilinopropenyl methyl ketone*, which separated from alcohol in almost colourless needles, m. p. 73° (Found: N, 5·7%). o-*Hydroxybenzylidene*-3 : 4-*dichloroaniline* crystallises from alcohol in long, yellow needles, m. p. 113°

(Found: N, 5·4%). The 3 : 4-dichloroaniline required was prepared by reducing the corresponding nitro-compound by the iron method.

o-*Anisidine.*—Condensation occurred readily to give β-o-*methoxyanilinopropenyl methyl ketone*, which separated from light petroleum (b. p. 40—60°) in plates, m. p. 51—52·5°.

3-*Chloro*-6-*acetamidoaniline.*—This also was found to condense with acetylacetone, but the product, like that from *o*-anisidine, was not further examined, since it gave no quinoline derivative when treated with concentrated sulphuric acid.

3 : 4-*Dichloro*-6-*nitroaniline.*—This base was recovered unchanged after being heated with excess of acetylacetone in a closed tube for 6 hours at 200°. The dichloro-base was readily obtainable by hydrolysing (90% sulphuric acid at 120° for 20 minutes) the corresponding acetyl derivative, the latter being prepared as described by Beilstein and Kurbatow (*Annalen*, 1879, **196**, 225).

Attempted Preparation of 2 : 3-*Dichloroaniline.*—(*a*) The nitration of 3 : 4-dichloroaniline in presence of a large excess of sulphuric acid led to a mixture of products, from which only unchanged base was isolated. It had been hoped that 3 : 4-dichloro-5-nitroaniline would be obtained, and thence, by removal of the amino-group, 2 : 3-dichloronitrobenzene. (*b*) *o*-Chloroacetanilide sulphonated readily when added to cold fuming sulphuric acid (25% SO_3). The solution was treated with nitric acid, and then evidently contained 3-chloro-5-nitro-4-acetamidobenzenesulphonic acid (compare D.R.-P. 206,345, dealing with a similar treatment of *m*-chloroacetanilide). The solution of the nitrosulphonic acid, when diluted slightly and boiled, contained acetic acid, but various methods tried did not give detectable quantities of 2-chloro-6-nitroaniline, from which it had been hoped to prepare 2 : 3-dichloronitrobenzene.

Conversion or Attempted Conversion of Anils of Acetylacetone into Substituted 2 : 4-*Dimethylquinolines.*—The most satisfactory method of effecting this condensation was as follows: The anil was slowly added, as a fine powder, or as a thin stream of liquid, to six times its weight of concentrated sulphuric acid, the latter being kept well shaken, and cooled below 5°. As soon as solution occurred, the mixture was heated for 0·5 hour on the boiling water-bath. The extent of condensation was readily diagnosed by diluting a little of the sulphuric acid solution. In cases of unsuccessful condensation, the odour of acetylacetone became apparent at once, and, usually, the sulphate of the unchanged base separated. Neither of these observations was made in the case of a successful condensation, and the further addition of potassium dichromate then gave an immediate precipitate of the quinoline dichromate

(see above under *p*-toluidine). The isolation of the quinolines presented no difficulty.

β-*Anilinopropenyl Methyl Ketone.*—The yield of pure 2 : 4-dimethylquinoline obtained was 90% on the weight of anil taken, or 75% on the weight of aniline. The success of this condensation appears to depend largely on the purity of the anil, the distillation of which (Combes, *loc. cit.*) is not only unnecessary, but disadvantageous.

The anils from acetylacetone and *o*- and *p*-chloroaniline, 2 : 4-, 2 : 5-, and 3 : 5-dichloroaniline, *o*-anisidine and 3-chloro-6-acetamidoaniline were not converted into the corresponding quinolines by the sulphuric acid method. Use of absolute sulphuric acid, or of slightly fuming acid, or variation of the temperature of heating made no difference to the result.

The anil from 2 : 5-dimethoxyaniline behaved exactly as described by Lions, Perkin, and Robinson (*loc. cit.*), the yield of 5 : 8-dimethoxy-2 : 4-dimethylquinoline being almost quantitative.

β-m-*Chloroanilinopropenyl Methyl Ketone.*—This anil (compare that last mentioned) was converted almost quantitatively into *7-chloro-2 : 4-dimethylquinoline*, the *hydrate* of which separated from aqueous alcohol in colourless needles, m. p. 61° (Found : Cl, 16·7. $C_{11}H_{10}NCl$ requires Cl, 18·5%. $C_{11}H_{10}NCl,H_2O$ requires Cl, 16·9%). Crystallisation of the hydrate from light petroleum afforded the anhydrous base in prismatic needles, m. p. 46·5—48·5° (Found : Cl, 17·9%). The quinoline is obtained in almost theoretical yield if the anil–sulphuric acid solution is heated, not at 100°, but at 130—140°.

7-Chloro-2 : 4-dimethylquinoline hydrochloride forms colourless needles, m. p. 277° (decomp.), soluble in water [Found : Cl (ionisable), 15·8. $C_{11}H_{10}NCl,HCl$ requires Cl (ionisable), 15·6%]. The *sulphate* separates from water in rhombohedra, and the *dichromate* in brilliant yellow needles. The *silver nitrate additive compound*, colourless needles [Found : Ag, 17·8. $(C_{11}H_{10}NCl)_2,AgNO_3$ requires Ag, 17·6%] melts at 197° (decomp.).

In an attempt to synthesise this quinoline, various experiments were carried out on the preparation of 4-chloro-2-aminoacetophenone. (1) This substance could not be isolated from the product of interaction of *p*-chloroaniline with acetic anhydride in presence of zinc chloride, although aniline, under similar conditions, is known to afford *p*-aminoacetophenone (Klingel, *Ber.*, 1885, **18**, 2688). (2) 2 : 4-Dinitroethylbenzene was not converted into 2 : 4-dinitroacetophenoneoxime when kept at room temperature in presence of amyl nitrite and piperidine, although Reich and Nicolaeva (*Helv. Chim. Acta*, 1919, **2**, 84) obtained a small yield of the oxime by using

sodium ethoxide as the condensing agent. (3) 2 : 4-*Dichloroacetophenone* was not converted into 4-chloro-2-aminoacetophenone when heated for 6 hours at 180° with alcoholic ammonia. The 2 : 4-dichloroacetophenone was obtained in 15% yield by condensing *m*-dichlorobenzene with acetyl chloride in presence of aluminium chloride. The majority of the dichlorobenzene was recovered unchanged. 2 : 4-Dichloroacetophenone has m. p. 33—34°, and b. p. 140—150°/15 mm. (Found: Cl, 37·2. $C_8H_6OCl_2$ requires Cl, 37·5%). To a boiling suspension of 1 g. of the ketone in 100 c.c. of 1·5% aqueous sodium hydroxide, were added 2·23 g. of potassium permanganate dissolved in 50 c.c. of water. Immediate oxidation occurred, and the sole product obtained, after crystallisation from aqueous alcohol, was 2 : 4-dichlorobenzoic acid, m. p. 161—162°.

β-3 : 4-*Dichloroanilinopropenyl Methyl Ketone.*—The only successful condensation of this compound was carried out by slowly adding the anil to five times its weight of cooled concentrated sulphuric acid, and heating the resulting solution at 130—140° for 4 hours. On cooling and pouring the mixture into water, a little 3 : 4-dichloroaniline sulphate separated; this was collected. The filtrate was rendered alkaline with ammonia, the precipitated quinoline was removed and dissolved in dilute sulphuric acid, and dilute potassium dichromate solution added. The precipitated *dichromate* (yellow needles, soluble in hot, but insoluble in cold water) was collected, and converted into the free base, which, after crystallisation from alcohol or light petroleum (b. p. 80—100°), formed colourless needles, m. p. 119—120° (Found: Cl, 31·5. $C_{11}H_9NCl_2$ requires Cl, 31·4%). Repetition of this condensation some dozen times under apparently similar conditions never gave rise on any second occasion to isolable quantities of the quinoline. Variation of the concentration of sulphuric acid, or of temperature or of time of heating, or of the conditions of mixing of anil and acid, also led to the same negative result. Saturation of a glacial acetic acid solution of the anil with dry hydrogen chloride (compare Bülow and Issler, *loc. cit.*) or treatment of a similar solution with acetic anhydride, or with acetyl chloride, did not cause ring-closure. The anil was also heated with syrupy phosphoric acid at 130—145° and then at 200° for 2 hours, but after this treatment, only 3 : 4-dichloroaniline was isolated. In the case of the acetyl chloride experiment, a crystalline solid separated after 5 minutes, but then redissolved. Treatment of the anil with a mixture of acetic anhydride and acetyl chloride merely led to the production of 3 : 4-dichloroacetanilide.

6 : 7-*Dichloro*-2 : 4-*dimethylquinoline hydrochloride* forms white needles, m. p. 235°, sparingly soluble in water [Found: Cl (ionisable), 13·6. $C_{11}H_9NCl_2,HCl$ requires Cl (ionisable), 13·5%]. The

chloroaurate forms twig-like, yellow needles, sparingly soluble even in hot water; the *sulphate* forms white needles; the *silver nitrate additive compound* is precipitated when an alcoholic solution of the base is treated with an aqueous solution of silver nitrate. It forms colourless needles, m. p. 218—219°, soluble in hot, but sparingly soluble in cold, alcohol [Found: Ag, 17·7. $(C_{11}H_9NCl_2)_2,AgNO_3$ requires Ag, 17·4%].

Nitration of 6 : 7-*Dichloro*-2 : 4-*dimethylquinoline.*—The method used for nitrating this base, and for all the other quinoline bases mentioned, unless otherwise stated, was as follows: The base was added slowly to five times its weight of a mixture, kept at −5°, of 1 part by weight of fuming nitric acid (*d* 1·5) and 2 parts by weight of concentrated sulphuric acid (*d* 1·84). The resulting solution was kept at the ordinary temperature for 1—2 hours and then poured on ice, and the nitro-compound was isolated either as the sulphate or as the free base.

In the case of 6 : 7-*dichloro*-8(?)-*nitro*-2 : 4-*dimethylquinoline*, the base was crystallised from alcohol, and then formed white needles, m. p. 197° (Found: N, 10·6. $C_{11}H_8O_2N_2Cl_2$ requires N, 10·4%). Nitration of 6 : 7-dichloro-2 : 4-dimethylquinoline with mixed acid at 60° also gave the nitro-compound described above.

Consideration of the other results obtained in this work suggests that the nitro-compound is of the 8- rather than of the 5-type.

Preparation of Substituted 2 : 4-*Dimethylquinolines by the Beyer Process.*—The method adopted was essentially that used by Beyer (*loc. cit.*), but in detail as follows: (*a*) A mixture of 96 g. of paraldehyde and 160 g. of acetone was saturated with dry hydrogen chloride, and left for 3 days. Such a mixture then weighed approximately 425 g. (*b*) The substituted aniline (1 mol.) was thoroughly ground with 3 mols. of concentrated hydrochloric acid, and the mixture added to one of 0·5 mol. of nitrobenzene and 255 g. of the acetone–paraldehyde–hydrogen chloride mixture. The whole was heated at 100° under reflux for 10 hours, and then worked up by an appropriate method, as described under individual compounds.

8-*Chloro*-2 : 4-*dimethylquinoline.*—The reaction mixture obtained from *o*-chloroaniline by the process just mentioned was poured into water; the resulting mixture was repeatedly extracted with ether, and the aqueous-acid layer rendered alkaline with sodium hydroxide. It was then thoroughly extracted with ether, and the ethereal extract was washed with brine and dried over anhydrous sodium sulphate. Evaporation of the ether and distillation of the residue under diminished pressure afforded two fractions, the first consisting of 40% of the original chloroaniline used; the second, b. p. 170—190°/15 mm. (mainly 185°/15 mm.), was 8-*chloro*-

2 : 4-*dimethylquinoline* (yield 25%), which solidified on cooling. After being twice crystallised from light petroleum (b. p. 40—60°), it formed stout, white prisms, m. p. 74° (Found : Cl, 18·6. $C_{11}H_{10}NCl$ requires Cl, 18·6%). The quinoline separates anhydrous from aqueous alcohol in small, rectangular plates. It was unaffected by piperidine after 1 hour's heating at 100°.

Nitration of 8-*Chloro*-2 : 4-*dimethylquinoline*.—The last-named quinoline nitrated readily, and on pouring the nitration mixture on ice a copious white precipitate of the *sulphate* of 8-chloro-5-nitro-2 : 4-dimethylquinoline was obtained. This was collected and treated with aqueous ammonia, and the reddish-brown solid obtained was crystallised from alcohol. The nitro-compound forms pale yellowish-brown prisms, m. p. 107—108° (Found : Cl, 15·1. $C_{11}H_9O_2N_2Cl$ requires Cl, 15·0%) (yield, more than 90%).

8-*Chloro*-5-*amino*-2 : 4-*dimethylquinoline* was prepared by the reduction of the 5-nitro-compound with iron, water, and ferric chloride. The reaction mixture was cooled and filtered. The residue of iron and amino-compound was dried and extracted with benzene. The *amino-compound* separated from the cooled benzene solution in brown prisms, m. p. 170—172° (Found : Cl, 17·1. $C_{11}H_{11}N_2Cl$ requires Cl, 17·2%) (yield, 33%).

Conversion of 8-*Chloro*-5-*amino- into* 5 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The chloroamino-compound (4 g.) was ground with 12 c.c. of concentrated hydrochloric acid, and the stiff reddish-brown paste so obtained cooled to −5°. A solution of 1·4 g. of sodium nitrite in 4·5 c.c. of water was slowly added. Diazotisation was rapid, and to the clear solution obtained was added a suspension of 5 g. of copper powder in hydrochloric acid (1 vol. of concentrated acid : 1 vol. of water). A brisk evolution of nitrogen occurred. Removal of the copper left a yellowish solution, which when treated with aqueous ammonia gave an almost theoretical yield of 5 : 8-dichloro-2 : 4-dimethylquinoline as a white precipitate. This, after being twice crystallised from alcohol, formed prismatic needles, m. p. 117—118°, alone or when mixed with 5 : 8-dichloro-2 : 4-dimethylquinoline prepared from 2 : 5-dichloroaniline (see below).

Chlorination of 8-*Chloro*-2 : 4-*dimethylquinoline*.—A solution of 1 g. of the quinoline in 20 c.c. of glacial acetic acid was heated at 60°, saturated with chlorine, and then treated with water. The white precipitate of the *tetrachloro*-compound obtained, after being twice crystallised from alcohol, formed slender needles, m. p. 150—152° (Found : Cl, 47·5. $C_{11}H_7NCl_4$ requires Cl, 48·1%).

6-*Chloro*-2 : 4-*dimethylquinoline*.—The Beyer reaction mixture from *p*-chloroaniline was poured into water, and the product was extracted with ether. The aqueous layer was evaporated to about one-third

of its original volume; a crystalline precipitate of crude hydrochloride was slowly deposited. This was collected, extracted with boiling acetone to remove colouring matter, and then treated with warm aqueous ammonia. The almost pure base so obtained separated from light petroleum (b. p. 80—100°) in stout prisms, m. p. 98—99° (Found: Cl, 16·4%) (yield, 16%). The quinoline crystallises from aqueous alcohol as the *hydrate*, silky needles, m. p. 84—85·5° (Found: Cl, 17·0. $C_{11}H_{10}NCl,H_2O$ requires Cl, 16·9%). The mother-liquor from which the above crude hydrochloride separated was found to contain only *p*-chloroaniline hydrochloride.

The quinoline forms an orange-yellow *dichromate*, which may be crystallised from water.

Nitration of 6-*Chloro*-2 : 4-*dimethylquinoline*.—The nitration mixture, when poured on ice, afforded a crystalline precipitate of the *sulphate* of 6-*chloro*-5-*nitro*-2 : 4-*dimethylquinoline*, which was filtered off and decomposed with warm aqueous ammonia. The practically pure base was then crystallised from alcohol, and formed canary-yellow prisms, m. p. 132—133° (Found: Cl, 15·8%) (yield over 90%). The chloronitro-compound was unaffected when heated for 10 minutes at 100° with excess of piperidine.

6-*Chloro*-5-*amino*-2 : 4-*dimethylquinoline*.—The preceding nitro-compound was reduced with iron powder, aqueous alcohol, and ferric chloride. The reaction mixture was filtered while still hot, the residual iron well washed with alcohol, and the alcoholic extracts and filtrate were evaporated. The solid that separated on cooling crystallised from benzene in pale yellow, prismatic needles, m. p. 131—133° (Found: Cl, 17·2%) (yield, 52%).

Conversion of 6-*Chloro*-5-*amino- into* 5 : 6-*Dichloro*-2 : 4-*dimethylquinoline*.—The base (9·1 g.) was ground with 30 c.c of concentrated hydrochloric acid, and the resulting canary-yellow hydrochloride paste was treated at −5° with a solution of 3·1 g. of sodium nitrite in 5 c.c. of water. Diazotisation was rapid, and to the clear solution so obtained copper and hydrochloric acid were added as usual. The whole assumed a dirty green colour, and suddenly set to a stiff paste. Two volumes of water were then added, the whole was heated to boiling and filtered, and the filtrate was cooled. The resulting yellowish-brown hydrochloride (prisms) was collected and digested with aqueous ammonia. The base so obtained (6 g.), after being crystallised first from alcohol and then from light petroleum (b. p. 80—100°), formed stout, colourless prisms, m. p. 119—120° (Found: Cl, 30·9. $C_{11}H_9NCl_2$ requires Cl, 31·4%). A mixture of this quinoline (then of unknown constitution) with the 6 : 7-dichloro-isomeride (also then of unknown constitution) melted at about 90°.

Chlorination of 6-*Chloro*-2 : 4-*dimethylquinoline*.—A solution, heated at 60°, of 1 g. (1 mol.) of the chloro-compound in 20 c.c. of glacial acetic acid containing 2·2 g. (5 mols.) of fused sodium acetate was saturated with chlorine. No precipitate was formed, but on dilution an oily *tetrachloro*-compound was thrown down. This became solid on standing, and after being crystallised from aqueous alcohol, and then from light petroleum (b. p. 40—60°), formed slender needles, m. p. 75·5—81° (Found: Cl, 48·4. $C_{11}H_7NCl_4$ requires Cl, 48·1%).

Nitration of 5 : 6-*Dichloro*-2 : 4-*dimethylquinoline*.—When the nitration mixture was poured on ice, the free base was precipitated. It crystallised from alcohol, in which it was very sparingly soluble, in silky needles, m. p. 151—152·5° (Found: Cl, 26·2. $C_{11}H_8O_2N_2Cl_2$ requires Cl, 26·2%) (yield, over 90%).

5 : 6-*Dichloro*-8(?)-*amino*-2 : 4-*dimethylquinoline*.—The preceding nitro-compound readily underwent reduction when heated with iron powder, aqueous alcohol, and a little hydrochloric acid. The mixture was finally filtered, the residue well washed with alcohol, and the alcoholic filtrates diluted with water. The precipitated amino-compound (yield, 83%) was dried, and then melted at 118—120° (Found: Cl, 27·6. $C_{11}H_{10}Cl_2N_2$ requires Cl, 29·5%). The crude base was used for the succeeding experiment.

Attempted Conversion of 5 : 6-*Dichloro*-8(?)-*amino*-2 : 4-*dimethylquinoline into* 5 : 6 : 8(?)-*Trichloro*-2 : 4-*dimethylquinoline*.—A suspension of the amino-compound in concentrated hydrochloric acid did not appear to undergo diazotisation when treated with sodium nitrite. Subsequent addition of copper caused no evolution of nitrogen.

Chlorination of 5 : 6-*Dichloro*-2 : 4-*dimethylquinoline*.—When chlorine was passed into a solution of 1·1 g. of the quinoline (1 mol.) in 30 c.c. of glacial acetic acid containing 1·23 g. (3 mols.) of fused sodium acetate, a precipitate of a *tetrachloro*-compound was formed. This separated from alcohol, in which it was very sparingly soluble, in slender needles, m. p. 157—158° (Found: Cl, 48·3. $C_{11}H_7NCl_4$ requires Cl, 48·1%). A mixture of the tetrachloro-compound with the tetrachloro-compound (m. p. 150—152°) obtained from 8-chloro-2 : 4-dimethylquinoline melted below 130°.

Preparation of 7-*Chloro*-2 : 4-*dimethylquinoline by the Beyer Method*.—The reaction mixture obtained from *m*-chloroaniline was poured into water, and the resulting mixture extracted several times with ether. The aqueous layer was basified, and extracted with ether, and the ethereal extract was washed with brine and dried. Distillation of the contained basic mixture under diminished pressure afforded 55% of unchanged *m*-chloroaniline as a first

fraction, and then a 36% yield of crude chloroquinoline, b. p. about 174°/10 mm. The latter partly crystallised on prolonged standing, and the crystalline portion, isolated on porous porcelain, separated from light petroleum (b. p. 40—60°) in prismatic needles, m. p. 42—45°, either alone or when mixed with the product from *m*-chloroaniline and acetylacetone (above). A little of the 5-isomeride was presumably present in the crude basic mixture, but in insufficient quantity for isolation.

7-Chloro-2 : 4-dimethylquinoline was unaffected by piperidine after 1 hour's heating at 100°.

Nitration of 7-Chloro-2 : 4-dimethylquinoline.—For this purpose, the chloro-compound obtained by the more convenient acetylacetone method was used. Nitration, followed by pouring on ice, gave a precipitate of the almost pure *7-chloro-8-nitro-2 : 4-dimethylquinoline* (yield over 95%). Nitration with warm mixed acid gave a similar result, either product separating from alcohol in slender, white needles, m. p. 189—189·5° (Found: N, 12·0. $C_{11}H_9O_2N_2Cl$ requires N, 11·8%).

When the nitro-compound was heated for 0·5 hour at 100° with an excess of piperidine, piperidine hydrochloride separated, and on extensive dilution with water a yellow powder was obtained. This separated from alcohol, in which it was sparingly soluble even when hot, in prisms; a second crystallisation from light petroleum (b. p. 80—100°)–benzene afforded *8-nitro-7-piperidino-2 : 4-dimethylquinoline* in rectangular plates, m. p. 168—170°. When mixed with the original chloronitro-compound, the substance melted at about 140°.

7-Chloro-8-amino-2 : 4-dimethylquinoline.—This substance, which was practically insoluble in hot aqueous alcohol, rapidly dissolved at 90—100° in that solvent in presence of iron powder and a little ferric chloride. Filtration, extraction of the iron powder with alcohol, and evaporation gave a black oil which solidified on cooling, and then crystallised from light petroleum (b. p. 40—60°) in slender, pale yellow needles, m. p. 51—53° (yield 83%) (Found: Cl, 17·4%).

Conversion of 7-Chloro-8-amino-2 : 4-dimethylquinoline into 7 : 8-Dichloro-2 : 4-dimethylquinoline.—The amino-compound was ground with concentrated hydrochloric acid, and the bright yellow hydrochloride paste diazotised at −10° with aqueous sodium nitrite. The clear red diazo-solution tended to undergo spontaneous decomposition, producing a coppery-brown, amorphous solid, but when it was added to a solution of cuprous chloride in hydrochloric acid normal decomposition appeared to occur. The product was treated with excess of ammonia, and the precipitated solid was collected, dried, and extracted with light petroleum (b. p. 40—60°). 7 : 8-

Dichloro-2 : 4-*dimethylquinoline* was then obtained in slender, prismatic needles, m. p. 104—104·5° (yield under 20%) (Found: Cl, 30·7%).

Chlorination of 7-*Chloro*-2 : 4-*dimethylquinoline*.—Chlorination of this base by the usual method in the cold afforded a *trichloro*-2 : 4-*dimethylquinoline*, which separated from alcohol in colourless needles, m. p. 195° (Found: Cl, 41·0. $C_{11}H_8NCl_3$ requires Cl, 40·9%).

6 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The condensation mixture obtained by applying the Beyer reaction to 2 : 4-dichloroaniline was poured into water, and the resulting mixture repeatedly extracted with ether. The aqueous layer was boiled until free from ether, and then basified. The solid precipitated, after being collected and dried, was extracted with hot light petroleum (b. p. 80—100°), from which solvent 6 : 8-dichloro-2 : 4-dimethylquinoline separated in slender needles, m. p. 148—148·5° (yield 20%) (Found: Cl, 31·4%). The base separated anhydrous from aqueous alcohol.

Nitration of 6 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The nitration solution when poured into a large bulk of water gave a precipitate of crude 6 : 8-*dichloro*-5(?)-*nitro*-2 : 4-*dimethylquinoline*, which separated from alcohol in pale yellow prisms, m. p. 120—122°. A further crystallisation from light petroleum (b. p. 40—100°) raised the m. p. to 122—123° (yield, 80%) (Found: Cl, 26·7%).

6 : 8-*Dichloro*-5(?)-*amino*-2 : 4-*dimethylquinoline*.—Reduction of the corresponding nitro-compound was effected by the usual method, using aqueous alcohol. The iron residue was extracted with hot acetone, and the extracts were evaporated. Crystallisation of the residue from alcohol afforded white, rectangular plates, m. p. 194—195° (yield, 81%) (Found: Cl, 29·6%). The amino-compound was converted by concentrated hydrochloric acid into a stiff, orange hydrochloride paste, which diazotised very slowly. Addition of copper powder caused some nitrogen evolution, but only unchanged base was isolated when the product was worked up.

Chlorination of 6 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—A solution of 1 g. of the quinoline (1 mol.) in 20 c.c. of glacial acetic acid containing 0·36 g. (1 mol.) of fused sodium acetate was heated at 60°, and saturated with chlorine. The precipitated solid separated from alcohol in needles, m. p. 124—125°, and was a *pentachloro*-quinoline. A mixture with the product obtained by the chlorination of 5 : 8-dichloro-2 : 4-dimethylquinoline (m. p. 127—128°) melted at 125—127°.

5 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The product of the Beyer condensation using 2 : 5-dichloroaniline was poured into a large bulk of water, and the black, oily layer separated. The aqueous

layer was treated in the usual manner, and finally gave the dichloroquinoline as a solid, which separated from alcohol or from light petroleum (b. p. 80—100°) in prismatic needles, m.p. 117—118·5° (yield, 29%) (Found: Cl, 31·5%).

5 : 8-*Dichloro*-6-*nitro*-2 : 4-*dimethylquinoline*.—Nitration of the preceding quinoline, followed by dilution, afforded a precipitate which, after treatment with ammonia, separated from alcohol, in which it was very sparingly soluble, in white, slender needles, m. p. 155—157°. It separated from benzene in prisms (yield, over 90%) (Found: Cl, 26·3%).

5 : 8-*Dichloro*-6-*amino*-2 : 4-*dimethylquinoline*.—The nitro-compound underwent reduction with the usual reagents, in presence of aqueous alcohol. The iron residue was extracted for several hours with boiling benzene, the latter then evaporated, and the residue crystallised from benzene; the amino-compound was then obtained in brown octahedra, m. p. 192—193° (yield, 40%) (Found: Cl, 29·5%).

Conversion of 5 : 8-*Dichloro*-6-*amino- into* 5 : 6 : 8-*Trichloro*-2 : 4-*dimethylquinoline*.—The base was converted by concentrated hydrochloric acid into a paste consisting of yellow leaflets, which underwent diazotisation with difficulty. Addition of copper caused nitrogen evolution. Dilute hydrochloric acid was added, and then benzene, the latter to remove a black, tarry by-product. The acid solution, after being basified, gave a small quantity of a dark solid, which was boiled in alcoholic solution with charcoal, and after this treatment separated from alcohol, and later from light petroleum (b. p. 80—100°), in needles, m. p. 111—112·5°. A mixture of this compound with 5 : 6 : 8-trichloro-2 : 4-dimethylquinoline (see below) melted at 112—113·5°.

Chlorination of 5 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—Chlorination of this base at 60° in glacial acetic acid in presence of sodium acetate (1 mol.) afforded a pentachloroquinoline derivative as a precipitate, which separated, after two crystallisations from alcohol, in slender needles, m. p. 127—128° (Found: Cl, 54·0. $C_{11}H_6NCl_5$ requires Cl, 53·9%).

Preparation of 6 : 7-*Dichloro*-2 : 4-*dimethylquinoline by Beyer's Process*.—The reaction product obtained from 3 : 4-dichloroaniline when worked up in the usual manner gave about 55% of unchanged dichloroaniline, and a fraction, b. p. 180—190°/15 mm., which was evidently a mixture of 5 : 6- and 6 : 7-dichloro-2 : 4-dimethylquinoline. Separation by crystallisation of the dichromates gave a product, m. p. 80—105°, which was converted into a mixture of hydrochlorides. The latter was crystallised from dilute hydrochloric acid, and the hydrochloride of the 6 : 7-base so obtained was

treated with alkali. Crystallisation of the product from light petroleum (b. p. 80—100°) afforded a substance, m. p. 119—120°, which did not depress the m. p. of the quinoline obtained from acetylacetone (Found: Cl, 31·5%).

5 : 7-*Dichloro*-2 : 4-*dimethylquinoline*.—The reaction mixture from the Beyer condensation, using 3 : 5-dichloroaniline, was treated in the usual manner. Basification of the final acid solution gave a solid which was purified only with difficulty, but after being crystallised from light petroleum (b. p. 80—100°) and then from light petroleum (b. p. 60—80°) formed small prisms, m. p. 84—86° (yield, 20%) (Found: Cl, 31·5%).

On the first occasion of attempting this preparation, the paraldehyde–acetone–hydrogen chloride mixture used had been prepared 2 months previously. Condensation, followed by pouring into a large bulk of water, gave a black oil containing suspended solid. This was filtered and pressed, and then thoroughly extracted with a mixture of equal volumes of benzene and light petroleum (b. p. 80—100°). After decantation of the cooled extract, a yellowish-brown solid separated (31 g. from 50 g. of the dichloroaniline). It crystallised from alcohol in yellow leaflets, m. p. 168—169° (Found: Cl, 41·9, 42·0%). This *substance*, which will be examined later, was converted by aqueous ammonia into a second *substance*, which separated from light petroleum (b. p. 40—100°) in bunches of colourless needles, m. p. 69—70° (Found: Cl, 36·5, 36·6%). The second substance readily dissolved in hot dilute mineral acids, the solutions depositing crystalline precipitates on cooling.

5 : 6 : 8-*Trichloro*-2 : 4-*dimethylquinoline*.—Beyer condensation with 2 : 4 : 5-trichloroaniline gave a product, which, on pouring into water, afforded tarry material containing a solid in suspension. The aqueous portion, when basified, deposited tarry material only. The above solid was extracted with boiling hydrochloric acid (concentrated acid : water, 1 : 1), and tar removed. On cooling, 2 : 4 : 5-trichloroaniline hydrochloride separated, and this was removed. The mother-liquor, on basification, afforded the crude trichloroquinoline, which then separated from alcohol and later from light petroleum (b. p. 80—100°) in small, prismatic needles, m. p. 113—114° (Found: Cl, 41·5. $C_{11}H_8NCl_3$ requires Cl, 40·9%). The quinoline does not form a hydrate, and when dissolved in the usual manner in a mixture of nitric and sulphuric acids remained unchanged.

Beyer Condensation with o-*Nitroaniline*.—The condensation product was treated in the usual manner. At the basification stage, a brown, tarry solid was obtained. This readily dissolved in hot alcohol to give a solution, which on cooling deposited crystals.

These dissolved only with difficulty in fresh hot alcohol, from which solvent a *substance* separated in prismatic needles, m. p. 145—147° (12 g. from 35 g. of *o*-nitroaniline).

Beyer Condensation with p-*Nitroaniline.*—The condensation product, when poured into water, deposited a black tar, which was rejected. The aqueous layer was repeatedly extracted with benzene, the latter removed, and alkali added. The *substance* so obtained then separated from alcohol in brownish leaflets, m. p. 159—162° (31 g. from 50 g. of *p*-nitroaniline). This compound and that obtained from *o*-nitroaniline are under investigation.

When *m*-nitroaniline was submitted to the Beyer condensation, only unchanged base was isolated. 3-Chloro-6-nitroaniline and 3 : 4-dichloro-6-nitroaniline, on the other hand, were converted into unworkable tarry products.

3 : 4-*Dichloroacetophenone.*—A mixture of 251 g. of *o*-dichlorobenzene and 229 g. of anhydrous aluminium chloride was slowly treated with 133 g. of acetyl chloride and then heated at 100° for 3 hours. The product was poured on ice, hydrochloric acid added, and the oily material extracted with carbon tetrachloride. Vacuum distillation afforded 130 g. of pure 3 : 4-*dichloroacetophenone*, b. p. 135°/12 mm. (yield, 40%). This became solid on cooling, and then separated from light petroleum (b. p. 80—100°) in bunches of white needles, m. p. 76° (Found: Cl, 37·6. $C_8H_6OCl_2$ requires Cl, 37·5%).

When 2 : 4 : 5-trichlorobenzene was treated in a similar manner, it was unaffected.

Nitration of 3 : 4-*Dichloroacetophenone.*—When the ketone was dissolved either in nitric acid (*d* 1·5) kept at 10—15°, or in a mixture of glacial acetic and fuming nitric acids, it was unaffected. When it was heated with the fuming acid at 50—55°, it was extensively oxidised. Addition of fuming nitric acid to a solution of the ketone in acetic anhydride at 60—70° effected no change. A mixture of fuming nitric and concentrated sulphuric acids at −10° did not affect the ketone, but at 15° caused resinification. A large number of variations of these experiments gave similar results. Finally, nitration was effected by the following method: The ketone was added in small portions to seven times its weight of nitric acid (*d* 1·5), the temperature being allowed to rise to 35—38°, but not above 40°. The solution was kept for 5 minutes, the temperature being maintained between 35° and 38°, and was then poured into a large bulk of water. 3 : 4-*Dichloro*-2-*nitroacetophenone* separated as a pale yellow solid, which was collected, washed, and crystallised from alcohol. It formed irregular plates, m. p. 100—102° (Found: Cl, 30·4. $C_8H_5O_3NCl_2$ requires Cl, 30·4%).

3 : 4-*Dichloro*-2-*aminoacetophenone*.—The nitro-compound underwent rapid and almost quantitative reduction when heated with iron powder, water, and a little ferric chloride. The cooled mixture was filtered, and the solid residue repeatedly extracted with benzene. After concentration of the extract, the amino-compound separated on cooling in yellow prisms, the m. p., 154—156°, of which was not affected by a further crystallisation from acetone (Found: Cl, 34·8. $C_8H_7ONCl_2$ requires Cl, 34·9%).

Condensation of 3 : 4-*Dichloro*-2-*aminoacetophenone with Acetone*.—(*a*) When the amino-compound was heated under reflux in acetone solution, together with a little piperidine, for 6 hours, it was unaffected. (*b*) A mixture of the amino-compound (1 g.), acetone (3 c.c.), and 50% aqueous sodium hydroxide (0·2 c.c.) was heated in a closed tube for 6 hours at 185°. When cold, the tube contained a mass of brown crystals. The contents of the tube were extracted with boiling acetone, the extract was filtered, and the acetone evaporated. The solid residue then crystallised from light petroleum (b. p. 80—100°) in slightly brown needles, m. p. 119—120°. The substance produced no depression of the m. p. of the products obtained by the acetylacetone and Beyer methods (from 3 : 4-dichloroaniline) and was 6 : 7-dichloro-2 : 4-dimethylquinoline. A mixture with 5 : 6-dichloro-2 : 4-dimethylquinoline melted below 90°.

Nitration of 2 : 4-*Dimethylquinoline*.—A solution of the quinoline (102 g.) in 510 g. of concentrated sulphuric acid was slowly treated at 5° with 290 g. of the usual mixture of nitric and sulphuric acids (*i.e.*, an excess for mononitration. Addition of the last half of the mixed acid caused no temperature rise). The solution was poured on ice, and the resulting clear solution basified with ammonia. The precipitated 8-*nitro*-2 : 4-*dimethylquinoline* crystallised from alcohol in brown needles, m. p. 118—119° (yield 93%) (Found: N, 13·7. $C_{11}H_{10}O_2N_2$ requires N, 13·8%).

8-*Amino*-2 : 4-*dimethylquinoline*.—Reduction of the preceding nitro-compound by means of iron powder, water, and ferric chloride proceeded vigorously, but the product was difficult to purify. Repeated extraction with light petroleum (b. p. 80—100°) gave a solution from which tarry matter separated on cooling. When no more tar separated, light petroleum (b. p. 40—60°) was added, whereupon the amino-compound separated in brownish-yellow plates, m. p. 89—92° (yield, 26 g.) (Found: N, 15·9. $C_{11}H_{12}N_2$ requires N, 16·3%). The *picrate* separates from alcohol in bunches of yellow prisms. The sulphate is bright yellow, and sparingly soluble in water. A dilute sulphuric acid suspension diazotised readily, but on heating, the resulting solution gave a product other than the expected hydroxy-compound.

Conversion of 8-Amino- into 8-Chloro-2 : 4-dimethylquinoline.—(*a*) The base was diazotised in hydrochloric acid suspension. Addition of cuprous chloride–hydrochloric acid solution gave an indefinite product. (*b*) The amino-compound (17 g.) was ground with 50 c.c. of concentrated hydrochloric acid, and the resulting orange-red paste treated slowly at −5° with a solution of 6·6 g. of sodium nitrite in 10 c.c. of water. Diazotisation proceeded rapidly, with the formation of a clear solution, to which a suspension of copper powder in hydrochloric acid was added. Nitrogen was at once evolved, and the mixture was diluted with water and filtered. Addition of excess of ammonia gave a gummy precipitate, which was dissolved in a hot mixture of 25 c.c. of concentrated sulphuric acid and 125 c.c. of water. On cooling, the sulphate of 8-chloro-2 : 4-dimethylquinoline separated in pale yellow needles, which were collected, and decomposed with ammonia. The base so obtained, after crystallisation from aqueous alcohol and then from light petroleum (b. p. 40—60°), melted at 74°. A mixture with the base obtained by the Beyer method using *o*-chloroaniline melted at the same temperature.

Condensation of Dibenzoylmethane with Aniline.—A mixture of dibenzoylmethane (1 mol.) and *freshly distilled* aniline (1·25 mols.) was boiled under reflux for 9 hours. On cooling, the whole became solid, and was fractionally crystallised from alcohol. Colourless plates, m. p. 161°, separated first, and these did not depress the m. p. of benzanilide (Found: N, 7·6. Calc.: N, 7·1%). The mother-liquor finally yielded a solid, which separated from benzene–light petroleum in bright yellow prisms, m. p. 102—103° (Found: N, 4·1; *M*, cryoscopic in benzene, 288. Calc.: N, 4·7%; *M*, 299). This substance is evidently identical with that described by Watson (*loc. cit.*).

A few of the experiments described above were carried out by Mr. R. J. W. Smith, M.Sc. The authors desire to acknowledge the receipt of grants from the Research Fund of the Chemical Society in aid of the investigation.

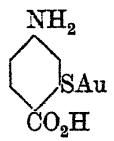
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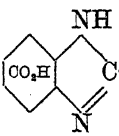
[*Received, May 11th*, 1927.]

CCXL.—*Gold and Mercury Derivatives of 2-Thiolglyoxalines. Mechanism of the Oxidation of 2-Thiolglyoxalines to Glyoxalines.*

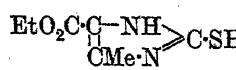
By ISIDORE ELKANAH BALABAN and HAROLD KING.

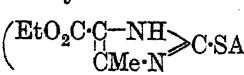
THE application of compounds of gold to the treatment of tuberculosis starts from an old observation by Koch that inhibition of the growth of tubercle bacilli by gold cyanogen compounds occurs at a dilution of 1 in 2 million, but the question as to the chemotherapeutic efficacy of organic gold compounds in tuberculosis is still an open one. Two organic compounds of gold have attained considerable prominence in Germany for the treatment of tuberculosis, namely, 4-amino-2-aurothiolbenzoic acid (krysolgan) (I) (D.R.-P. 349012) and 2-aurothiolbenziminazolecarboxylic acid (triphal) (II) (E.P. 225875 of 1923), but there is no record of the cure of experimental infections of tuberculosis in animals by these substances.

(I.) 

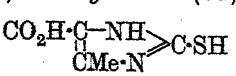
(II.) 

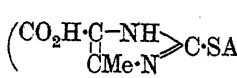
Both substances belong to a common type, of which an indefinite number could be prepared by synthesis, and the present communication is an attempt to determine whether there is any curative action, on experimental tuberculosis in animals, in this type of compound which would justify an extensive programme of syntheses in this field. For this purpose, ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (III) has been chosen as a starting point, as it is fairly readily accessible from ethyl acetoacetate.

(III.) 

(IV.) 

When treated in methyl-alcoholic solution with auric chloride (1/3 mol.), it yields together with other products *ethyl 2-aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate* (IV), from which the carboxylic acid cannot be obtained without decomposition and separation of gold. The ester (III) can, however, be hydrolysed to *2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid* (V), which under similar conditions yields *2-aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid* (VI).

(V.) 

(VI.) 

The action of auric chloride on mercaptans was first studied by Zeise (*Ann. Physik*, 1834, **31**, 369), who, from the analysis of the amorphous product, C_2H_5SAu, of the action of auric chloride on ethyl mercaptan, considered that two atoms of chlorine were set free which acted on another portion of the mercaptan. In agreement with this, Hermann (*Ber.*, 1905, **38**, 2813), who examined the action of auric chloride on benzyl and *iso*amyl mercaptans, found the optimum conditions to be given by the equation

$$AuCl_3 + 3R{\cdot}SH = R{\cdot}SAu + RS{\cdot}SR + 3HCl.$$

The auromercaptides were amorphous and the disulphides were definitely identified.

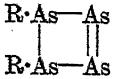
In the present instance, although the optimum conditions are determined by three molecular proportions of the thiolglyoxaline to one of auric chloride, the disulphide which should be produced in this reaction was never found, but only unchanged thiol acid. There is no doubt that the disulphide is initially produced, but, owing to the ease with which it acts as an acceptor for hydrogen, it is reduced during the subsequent operations necessary for its isolation. Attempts to make use of this ease of reversion of the disulphide to the thiol state, by using thiol acid and auric chloride in equimolecular proportion, to simplify the preparation of the 2-aurothiol acid (VI) which can be separated from the 2-thiol acid (V) only by a repetitive salting-out of the amorphous sodium salt of the aurothiol acid, were quite unsuccessful.

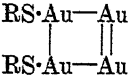
When auric chloride in methyl alcohol is added to the above-named thiolglyoxalines in methyl alcohol, there is invariably produced an intense blood-red coloration which persists for about 30 minutes and then fades to a pale yellow. There is no separation of gold. The same reaction is observed in aqueous hydrochloric acid solutions. It was first noted without comment by Gabriel and Pinkus (*Ber.*, 1893, **26**, 2203) for 2-thiol-4(or 5)-methylglyoxaline and by Tanret (*Compt. rend.*, 1909, **149**, 222) for ergothioneine, shown by Barger and Ewins (J., 1911, **99**, 2336) to be identical with 2-thiolhistidinebetaine. It is not, however, given by cysteine, thiocarbamide, allylthiocarbamide, or *p*-thiolphenylethylamine. We are not able to adduce any conclusive evidence as to the nature of this blood-red coloration. Whilst all the 2-thiolglyoxalines examined give the reaction instantaneously, 4(or 5)-*carbethoxy*-5(or 4)-*methylglyoxaline*-2-*disulphide* in methyl-alcoholic solution does not give it at once, but the colour gradually develops, lasts for many hours, and finally disappears. In hydrochloric acid solution the disulphide remains yellow for a few seconds on addition of chloroauric acid and then gives an amorphous, red precipitate

which becomes pale yellow after a few hours. One possibility is that the colour is due to the chromophoric influence of the sulphur atom on intermediate addition compounds of auric chloride with the thiolglyoxalines which gradually disappear as the auric chloride is used up in its reactions with the thiol group. This is supported by the observations of Wohl and Marckwald (*Ber.*, 1889, **22**, 1355), who found that platinum and gold chlorides formed with 2-thiol-1-methylglyoxaline brick-red and deep purple-red crystalline addition compounds, respectively, of the types, 2 base + $PtCl_4$, and base + $AuCl_3$, and of the present authors that the salt of 2-*ethylthiol*-4(or 5)-*methylglyoxaline* with chloroauric acid is red, whereas the addition compound of 2-phenyl-1-methylglyoxaline and auric chloride of the type base + $AuCl_3$ is deep yellow (J., 1926, 589). The other possibility is that the blood-red coloration is due to the transient formation of the free aurous radicals, R·SAu<, which polymerise to form the pale yellow auromercaptides R·SAu:AuS·R or, in general, $(R{\cdot}S{\cdot}Au<)_n$. The properties of these auromercaptides are in agreement with this formulation: they are all amorphous substances with well-marked colloidal properties.

In the reaction of only one other reducing agent with auric solutions have we observed a transient red coloration. In the preparation of sodium gold thiosulphate, $Na_3Au(S_2O_3)_2$, by the action of a neutral solution of gold chloride on sodium thiosulphate, a transient red colour is obtained which, examined spectroscopically, has a similar general absorption in the visible region to the blood-red colour obtained with thiolglyoxalines. In this case also, the reaction is essentially a reduction to the aurous state. Brown's view (*J. Amer. Chem. Soc.*, 1927, **49**, 959) that the colour is due to the formation of sodium aurate does not tally with the colour of alkali aurates, which are pale yellow or pale green.

2-Aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (VI) prepared as described above invariably contains an excess of combined gold in the approximate ratio of N:Au = 2 : 1·08 which finds a ready interpretation by analogy with the arsenicals. Just as over-reduction of arsinic acids leads to production of polyarsenides, which are usually formulated as in (VII), so here the product probably contains (VIII).

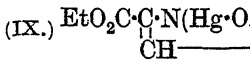
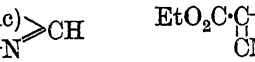
(VII.)




(VIII.)

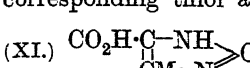
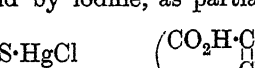
The reaction of thiolglyoxalines with mercuric salts is in striking contrast to their behaviour towards auric chloride. When ethyl glyoxaline-4(or 5)-carboxylate is digested in alcoholic solution with mercuric acetate, it yields *ethyl* 1-*acetoxymercuriglyoxaline*-4(or 5)-

carboxylate (IX) quantitatively, but ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate and the corresponding carboxylic acid, when digested with excess of mercuric chloride, yield *ethyl*

(IX.)   (X.)

2-*chloromercurithiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate* (X) and 2-*chloromercurithiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic acid* (XI) respectively. These are crystalline compounds and their constitution follows from their behaviour towards sodium hydroxide and ammonium sulphide.

Results of considerable interest have been obtained in an attempt to prepare the disulphide (XII) which should have arisen in the action of auric chloride on 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V). It cannot be obtained by oxidation of the corresponding thiol acid by iodine, as partial replacement of the

(XI.)   (XII.)

carboxyl group by iodine takes place, and it is not formed when 4(or 5)-*carbethoxy*-5(or 4)-*methylglyoxaline*-2-*disulphide* (XIII), prepared by the action of iodine upon ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate, is hydrolysed by alkalis or acids. After this ester disulphide (XIII) had been boiled for an hour with 10% aqueous sodium carbonate, the products isolated were 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V), the corresponding decarboxylated product 2-thiol-4(or 5)-methylglyoxaline, ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (III), and sulphur dioxide. On acid hydrolysis, 2-thiol-4(or 5)-methylglyoxaline was also obtained with other substances. Quantitative estimation of the sulphur dioxide produced showed that 74% of that required by the equation $2RS{\cdot}SR + 2H_2O = 3R{\cdot}SH + RH + SO_2$ was present. The mother-liquor contained sulphate, so that the deficiency in sulphur dioxide is probably accounted for by the reducing action of sodium sulphite on the disulphide, for the disulphide (XIII) is readily reduced to the thiol ester in aqueous solution by sulphur dioxide.

It seems probable that an unstable sulphinic acid is the intermediate product in the above hydrolysis, in which case the reaction would be the reverse of the mode of synthesis of disulphides of Otto and Schiller (*Ber.*, 1876, **9**, 1589):

$$3R{\cdot}SH + R{\cdot}SO_2H = 2RS{\cdot}SR + 2H_2O.$$

In support of this view, the first sulphinic acid in the glyoxaline series has been prepared and proves to be a very unstable substance

readily yielding sulphur dioxide at room temperature. When 2-thiol-4(or 5)-methylglyoxaline (XIV) is added at 0° to 10% hydrogen peroxide (2 mols.), it is converted for the most part into 4(or 5)-*methylglyoxaline-2-sulphinic acid* (XV) with simultaneous formation of small quantities of 4(or 5)-*methylglyoxaline-2-sulphonic acid* (XVI), 4(or 5)-methylglyoxaline, and sulphuric acid.

(XIII.) $\left(\begin{array}{l}EtO_2C\cdot C\text{—}NH\\ \quad\|\quad\quad\rangle C\cdot S\text{—}\\ CMe\cdot N\end{array}\right)_2$ $\begin{array}{l}CMe\cdot NH\\ \|\quad\rangle C\cdot SH\\ CH\text{—}N\end{array}$ (XIV.)

(XV.) $\begin{array}{l}CMe\cdot NH\\ \|\quad\rangle C\cdot SO_2H\\ CH\text{—}N\end{array}$ $\begin{array}{l}CMe\cdot NH\\ \|\quad\rangle C\cdot SO_3H\\ CH\text{—}N\end{array}$ (XVI.)

The sulphinic acid is a crystalline solid, stable at 0°. It has an acid reaction, but at room temperature it changes after a few hours into a strongly basic liquid containing 4(or 5)-methylglyoxaline and its *sulphite*. It consumes one atom of oxygen when titrated with permanganate at 0°, and is converted by excess of hydrogen peroxide, preferably in the presence of alkali, into the sulphonic acid. The formation of this unstable sulphinic acid is, in fact, exactly analogous to the formation of the somewhat more stable aminoiminomethanesulphinic acid, $NH{:}C(NH_2)\cdot SO_2H$, by the oxidation at 0° of thiocarbamide by hydrogen peroxide (Barnett, J., 1910, **97**, 63).

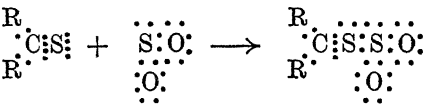
The instability of the glyoxalinesulphinic acid affords a satisfactory interpretation of the desulphuration of 2-thiolglyoxalines by means of nitric acid discovered by Wohl and Marckwald (*Ber.*, 1889, **22**, 575). These authors postulated the formation of an unstable sulphonic acid which was hydrolysed even under the conditions of oxidation:

$$N{:}C(SH)\cdot NH- \longrightarrow -N{:}C(SO_3H)\cdot NH- \longrightarrow -N{:}CH\cdot NH- + H_2SO_4.$$

This explanation was, however, disproved by the observations of Anschütz and Schwickerath (*Annalen*, 1895, **284**, 9), Biltz and Krebs (*ibid.*, 1912, **391**, 203), and Lamb and Pyman (J., 1924, **125**, 707). Biltz and Krebs favoured the view that disulphides are the intermediate products, but the results are much more compatible with the view that an unstable sulphinic acid is formed, and the more unstable it is, the smaller the proportion of sulphonic acid formed in the oxidation and the larger the proportion of desulphurised glyoxaline.

When the alkaline hydrolysate of 4(or 5)-carbethoxy-5(or 4)-methylglyoxaline-2-disulphide (XIII) is acidified to Congo-paper, the solution turns yellow and evolves sulphur dioxide. On removal of this by aspiration, the yellow colour vanishes, but it is restored when sulphur dioxide is passed into the solution. This has been traced to the formation of unstable, yellow or orange-yellow addition

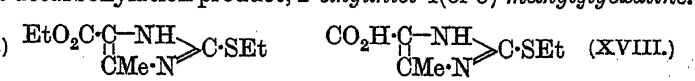
compounds between many 2-thiolglyoxalines and sulphur dioxide in aqueous or acid solution or in the dry state. Quantitative measurement of the amount of sulphur dioxide absorbed by dry 2-thiol-1-phenylglyoxaline showed that exactly one molecule is absorbed under one atmosphere of sulphur dioxide, but on exposure to the air the compound has a half-life period of 10 minutes. The reaction is also given by thiocarbamide, and is strikingly shown by allylthiocarbamide and 2-thiol-1 : 4-dimethylglyoxaline, which are immediately converted into yellow and orange-yellow liquids, respectively, by exposure to sulphur dioxide. The constitution of these labile addition compounds is best interpreted as a simple addition of the sulphur atom of the thiol group to the electromeric modification of sulphur dioxide containing two semi-polar double bonds.



This interpretation does not discriminate between the –NH·C(SH):N– structure and the –NH·CS·NH– structure of 2-thiolglyoxalines. Korczyński and Glebocka (*Gazzetta*, 1920, **50**, i, 378) have described a number of addition compounds of sulphur dioxide with a variety of amines, including thiocarbamide, and attribute their formation to the secondary valencies of the nitrogen atom. Ethyl 4(or 5)-glyoxalinecarboxylate, however, does not add on sulphur dioxide, so that their interpretation does not hold here.

The similarity between thiocarbamides and 2-thiolglyoxalines in their behaviour towards sulphur dioxide extends to the colour reaction described by Sato (*Biochem. Z.*, 1909, **23**, 45) for thiocarbamides, and an improved form of the test is described in the experimental portion together with a number of other colour reactions which may prove of service in this field.

In order to characterise 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V) more fully, it has been converted by esterification by alcoholic hydrogen chloride (compare Burtles, Pyman, and Roylance, J., 1925, **127**, 588) into *ethyl 2-ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate* (XVII), which on hydrolysis yields 2-*ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic acid* (XVIII) and its decarboxylation product, 2-*ethylthiol*-4(or 5)-*methylglyoxaline*.



The acid (XVIII) forms a *monohydrochloride* and a *semihydrochloride* and thus resembles some of the amino-acids, such as glycine and *dl*-alanine, which form normal and semi-hydrochlorides,

and the many anomalous amine salts recorded by Werner (*Ber.*, 1903, **36**, 149). The majority of these were formulated by Werner in terms of co-ordinated hydrogen : $XH + 2NR_3 = X{\cdot}H\begin{matrix}\diagup NR_3\\ \diagdown NR_3\end{matrix}$, which on the electronic theory of valency would be readily interpreted as

$$XH + 2R{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\overset{R}{\underset{R}{N}}}}{:} = \left[R{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\overset{R}{\underset{R}{N}}}}{:}H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\overset{R}{\underset{R}{N}}}}{:}R\right]^{+} X^{-}.$$

The case is in fact the parallel of the interpretation put forward for potassium hydrogen fluoride, KHF_2, where, however, co-ordinated hydrogen links the fluorine atoms in a negatively charged complex (Lewis, " Valence," 1923, 110). A difficulty, however, arises in the interpretation of the compounds $(NH_3)_4$,HCl (Joannis, *Compt. rend.*, 1902, **135**, 1106), $(NH_3)_4$,HBr (Bakhuis-Roozeboom, *Rec. trav. chim.*, 1885, **4**, 361), and $(NH_3)_4$,HNO_3 (Kuriloff, *Z. physikal. Chem.*, 1898, **25**, 108). These would indicate a co-ordination number of 4 for hydrogen or else chain formation of ammonia molecules with links of co-ordinated hydrogen.

We are indebted to Captain S. R. Douglas, F.R.S., for a determination of the effect of sodium aurothiolmethylglyoxalinecarboxylate on tubercle bacilli. It inhibits the growth of these organisms *in vitro* at a dilution of 1 in 100,000 (not tested at lower concentrations). Guinea-pigs were injected each with 0·5 mg. of a virulent culture of tubercle bacilli which had been subjected for 12 hours to a concentration of the sodium salt ranging from 1 in 1,000,000 to 1 in 1000. The time elapsing between injection and death of the animal from tuberculosis was progressively longer with increasing concentration of the salt used in the preliminary treatment of the bacilli. In no case had sterilisation been effected. Rabbits inoculated with a virulent strain were injected weekly with the sodium salt (0·01 g. per kilo.) and after four injections the lungs showed less signs of tubercular lesions than the controls, whilst the death of mice inoculated with the bacilli was distinctly delayed by one and by two injections of the sodium salt, 50 mice being used as controls, 25 mice for one dose and 25 for two doses.

To Miss Durham and Miss Marchal we are indebted for a determination of the toxicities to mice of sodium aurothiolmethylglyoxalinecarboxylate (0·05 mg. per g.) and of sodium 2-chloromercurithiolmethylglyoxalinecarboxylate (0·005 mg. per g.). The same compounds were tested for curative action on mice infected with trypanosomes, but no such action was detected.

Our thanks are also due to Professor F. L. Pyman, F.R.S., for the gift of samples of a series of thiolglyoxalines from his unique collection.

EXPERIMENTAL.

Hydrolysis of Ethyl 2-Thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (III).—This ester was prepared in 42% yield from ethyl acetoacetate as described by Posner and Gabriel (*Ber.*, 1894, **27**, 1141), but Wolff's method (*Annalen*, 1902, **325**, 135) was used for the preparation of oximinoacetoacetic ester. It melts at 236—237° (P. and G. give 229°) and is soluble in 64 parts of boiling water.

The ester (50 g.) was boiled for 1 hour with 100 g. of sodium carbonate (anhydrous) in 1000 c.c. of water, and the reaction then adjusted to neutrality to Congo-paper. The precipitate and the successive crops obtained by evaporation of the mother-liquors (in all, 38·3 g.) were extracted with one-half saturated sodium hydrogen carbonate solution, which removed the whole of the carboxylic acid and the major portion of the decarboxylated base, leaving behind non-hydrolysed ester mixed with a little decarboxylated base. The main alkaline extract on neutralisation to Congo-paper gave the carboxylic acid (23·35 g.), and the mother-liquors on concentration gave the thiol base (3·7 g.). The portion insoluble in sodium hydrogen carbonate solution (9·05 g.) was boiled with water (50 c.c.) and left, undissolved, almost pure ester (3·5 g.); the water-soluble fraction was made alkaline with sodium carbonate and boiled down in an open flask to hydrolyse the ester still present. From this alkaline liquor the thiol base was recovered in successive crops, 6·0 g. in all, the mother-liquors which gave the thiol base (3·7 g.) being incorporated at one stage. The final liquor was acidified to Congo-paper and gave a small crop of carboxylic acid (0·4 g.).

2-Thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V) is soluble in 100 parts of boiling water and separates in granular crystals. It melts with loss of carbon dioxide at 240—241°, and the crystalline residue obtained, at 244—245°, the m. p. of 2-thiol-4(5)-methylglyoxaline (Found: S, 20·5; N, 17·9. $C_5H_6O_2N_2S$ requires S, 20·3; N, 17·2%). The acid gives an immediate red colour with Pauly's reagent in sodium carbonate solution.

Esterification of 2-Thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic Acid.—The acid (5 g.) was suspended in 100 c.c. of absolute alcohol, and the liquid saturated with hydrogen chloride at 0°. The suspension was then boiled for 3 hours with further passage of the gas. After removal of alcohol and excess of acid by evaporation with water, the syrupy residue was dissolved in 20 c.c. of water and treated with saturated potassium carbonate solution so long as a crystalline precipitate separated. This amounted to 4·4 g., and

when crystallised from the minimum volume (350 c.c.) of boiling water separated in long, white, silky needles (4·05 g.), m. p. 144—145°.

Ethyl 2-*ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate* (XVII) is readily soluble in boiling organic solvents, but crystallises conveniently only from acetone, ethyl acetate, or water (Found in air-dried material: loss at 100°, 10·7. $C_7H_{10}O_2N_2S,1\frac{1}{2}H_2O$ requires H_2O, 11·2%. Found in anhydrous solid: N, 12·8. $C_7H_{10}O_2N_2S$ requires N, 13·1%). It forms very soluble salts with nitric, hydrochloric and sulphuric acids, the *hydrochloride* crystallising in needles. It forms an oily *chloroaurate*, but a *picrate* crystallising in glistening, yellow prisms, m. p. 135—136° (Found: picric acid by nitron, 52·1. $C_9H_{14}O_2N_2S,C_6H_3O_7N_3$ requires picric acid, 51·7%).

In a preliminary experiment (1·6 g. of thiol acid) where esterification was only carried out for 90 minutes, the product precipitated at neutrality (1·35 g.) gave by ether extraction 1·25 g. of *S*-ethyl ether and 0·1 g. of insoluble material which proved to be ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate.

S-*Alkylation of Ethyl* 2-*Thiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate*.—The 2-thiolcarboxylic ester (10 g.) was suspended in 100 c.c. of absolute alcohol and submitted to the same treatment as in the foregoing esterification. The yield of crude *S*-ethyl ether was 10·8 g. It was recrystallised from 100 volumes of boiling water and gave 10·3 g. of pure material crystallising in needles, m. p. 144—145°. On prolonged standing, the mother-liquor deposited stout, triangular plates which proved to be the same substance, m. p. 143—144°.

Alkaline Hydrolysis of Ethyl 2-*Ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate*.—The ethyl ester of the *S*-ethyl ether (8·1 g.) was boiled for 4 hours with 16·2 g. of anhydrous sodium carbonate in 162 c.c. of water. The ethereal extract on evaporation gave 2·3 g. of 2-*ethylthiol*-4(or 5)-*methylglyoxaline*, m. p. 68—69°. This base was insoluble in light petroleum and very soluble in benzene, and crystallised well from ethyl ether in delicate, rectangular leaflets, m. p. 69—71°. It was converted into the *picrate* (5·5 g.), which was soluble to the extent of 2·3% in boiling water and separated on cooling in prismatic needles, m. p. 136—137° (Found: picric acid by nitron, 62·6, 62·7. $C_6H_{10}N_2S,C_6H_3O_7N_3$ requires picric acid, 61·7%). The picrate was converted into the hydrochloride, which could not be crystallised, and a portion of the latter precipitated with chloroauric acid. The *chloroaurate* separated in red plates, m. p. 130—131° without decomposition (Found: Au, 41·0. $C_6H_{10}N_2S,HAuCl_4$ requires Au, 40·9%).

The alkaline liquors after ethereal extraction were made very

faintly acid to Congo-paper and concentrated; two crops of needles, 4·05 g. in all, were then obtained. Of this, 3·3 g. were dissolved in 10 c.c. of boiling water in a covered vessel to avoid access of nuclei from the air. When the solution was cool and supersaturated, it was inoculated with nuclei of the needles. The crop of needles (2·3 g.) was collected and washed with ice-cold water [Found: Cl, 8·3; N, 13·4. $(C_7H_{10}O_2N_2S)_2,HCl$ requires Cl, 8·7; N, 13·7%]. This *semihydrochloride* of *2-ethylthiol-4*(or 5)-*methylglyoxaline-5*(or 4)-*carboxylic acid* was very readily soluble in water, with a reaction faintly acid to Congo-paper. It melted rather indefinitely with effervescence between 122° and 125°, but without loss of carbon dioxide, as the residue did not give a picrate. If a strong aqueous solution was heated, the free *carboxylic acid* (XVIII) separated in stout rhombs; on cooling, needles of the semi-hydrochloride invariably separated, but the rhombs, even on prolonged standing, remained unchanged. If alkali was added until the faint acidity to Congo-paper was completely removed and the reaction was very faintly acid to sensitive methyl-orange paper, the free carboxylic acid was precipitated. It was soluble in 10 parts of boiling water and crystallised in large, rectangular tablets, m. p. 179—180° (efferv.) (Found: N, 14·9. $C_7H_{10}O_2N_2S$ requires N, 15·0%). The decarboxylated melt solidified and melted at 67° and gave a picrate identical with 2-ethylthiol-4(or 5)-methylglyoxaline picrate.

If the semi-hydrochloride (0·2 g.) be dissolved in a few drops of hot 3*N*-hydrochloric acid it forms a syrupy solution which soon deposits large, triangular prisms of the *monohydrochloride*, m. p. 189—190° (efferv.) (Found: Loss at 100°, 7·8. $C_7H_{10}O_2N_2S,HCl,H_2O$ requires H_2O, 7·5%. Found in dried salt: Cl, 16·0. $C_7H_{10}O_2N_2S,HCl$ requires Cl, 15·9%). This salt is very soluble in water, the solution turning Congo-paper blue.

Preparation of 5(or 4)-*Carbethoxy*-4-(or 5)-*methyl*-2-*glyoxaline Disulphide* (XIII).—Ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (1 g.) was dissolved in 1000 c.c. of hot water, cooled to 50°, and treated with *N*/10-iodine solution until a slight excess was present as shown by the pale brown colour. Usually 55 c.c. were required instead of the theoretical 53·7 c.c. Three further batches were treated similarly. The *disulphide* (3·25 g.) which separated during the addition of iodine was collected; the mother-liquors, on being again treated with iodine until present in slight excess, and then neutralised with sodium carbonate, deposited a further 0·2 g. of disulphide. The product (yield, 86%), m. p. 220—222°, separated from boiling alcohol (120 c.c.) as a voluminous felt of pale yellow needles; after a further crystallisation, the m. p. was con-

stant at 222—223° (yield, 3·25 g.) (Found : N, 15·3. $C_{14}H_{18}O_4N_4S_2$ requires N, 15·1%). The same ester with the same m. p. was obtained by oxidation of the thiol ester in alkaline solution with potassium ferricyanide, but it was difficult to free it from Prussian blue, formed in traces. It was also obtained by dissolving the thiol ester in spirit, adding a lump of fused sodium nitrite, and running *N*-sulphuric acid on to the nitrite so that there was a vigorous evolution of gases through the liquid. The solution eventually deposited the disulphide. A modification of this method may prove to be the most accessible route to this disulphide. In sodium carbonate solution, the disulphide gives a yellow colour with Pauly's reagent. The ester is readily reduced to the thiol ester by passage of sulphur dioxide in aqueous solution.

Hydrolysis of the Disulphide.—(a) *By alkali.* The disulphide (7·4 g.) was boiled for 1 hour with 15 g. of anhydrous sodium carbonate in 150 c.c. of water. The solution, on being neutralised to Congo-paper, turned yellow, evolved sulphur dioxide, and gave a fraction (2·95 g.). On concentration, two further fractions (0·45 and 1·6 g.) were obtained. The sodium hydrogen carbonate extracts of these fractions gave, on neutralisation to Congo-paper, 2·76 g. of 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid, identical in all its reactions with the product of hydrolysis of the corresponding 2-thiol ester. The portion soluble in sodium hydrogen carbonate but not precipitated on neutralisation was isolated by concentration and proved to be pure 2-thiol-4(or 5)-methylglyoxaline (0·1 g.), m. p. 244—245°. The portion of original material insoluble in sodium hydrogen carbonate, on three crystallisations from water, gave 0·4 g. of ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate, m. p. 237°.

Quantitative determinations of the proportion of sulphur dioxide formed in the hydrolysis of the disulphide were made by hydrolysing 1·23 g. (*M*/300) with 2·46 g. of anhydrous sodium carbonate in 24·6 c.c. of water for 1 hour at 100°. The alcoholic distillate contained only a trace of reducing substance, possibly acetaldehyde. The alkaline mother-liquor was made acid by addition of 3*N*-hydrochloric acid, and the liberated sulphur dioxide absorbed by aspiration into standard *N*/10-iodine solution, any volatile iodine being caught in *N*/10-sodium thiosulphate solution. In two separate experiments, 72·4 and 73·5% of the sulphur dioxide required by the equation $2RS{\cdot}SR + 2H_2O = SO_2 + RH + 3RSH$ was found. The mother-liquors also contained appreciable amounts of sulphate. The method of estimation was controlled by experiments on standard sodium sulphite solution and found to agree within 2%.

(b) *By acid.* The disulphide (0·9 g.) was boiled for 3 hours with

10 c.c. of 16% hydrochloric acid. The solution was evaporated dry at 50°, and the residue was dissolved in a little water and made faintly alkaline to litmus; an amorphous base (0·4 g.) then separated. This was probably a mixture of bases, as it did not behave normally on reduction to the thiol base with sulphur dioxide or on oxidation to a base free from sulphur by dilute nitric acid. After removal of the amorphous substance, the mother-liquors, on concentration, gave 0·2 g. of crude 2-thiol-4(or 5)-methylglyoxaline, m. p. 239°. Recrystallised from 1·2 c.c. of hot water, it separated in the characteristic large crystals of the pure thiol base, m. p. 244°.

Preparation of Ethyl 2-Aurothiol-4(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate* (IV).—Ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (1·86 g.; 3 mols.) in 100 c.c. of dry methyl alcohol was treated with 1 g. (1 mol.) of gold trichloride in 30 c.c. of methyl alcohol. The solution became brilliant ruby-red and after 2 hours was pale yellow. The alcohol was removed and treatment of the residue with 400 c.c. of boiling water left 0·22 g., m. p. 254° (decomp.), undissolved. On keeping, the solution deposited needles (1·35 g.), m. p. 170°, containing 30·3% of combined gold. These were extracted with a further 150 c.c. of boiling water, which left 0·35 g. of solid undissolved, m. p. 252° (decomp.). This was the required *ethyl 2-aurothiol-4*(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate* (Found: Au, 50·6. $C_7H_9O_2N_2SAu$ requires Au, 51·6%). Attempts to convert this ester into the corresponding acid by hydrolysis led to decomposition with separation of gold.

Preparation of 2-*Aurothiol-4*(or 5)-*methylglyoxaline-5*(or 4)-*carboxylic Acid* (VI).—2-Thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (4·7 g.), dissolved in 435 c.c. of pure dry methyl alcohol, was treated with 3·0 g. (1/3 mol.) of gold trichloride in 10 c.c. of methyl alcohol. After 1 hour, the deep ruby-red colour which developed immediately on mixing had completely gone. The yellow solution was concentrated to about 10 c.c. and diluted with 250 c.c. of water. The solution set to a jelly which rapidly broke up with deposition of a mixture of amorphous and crystalline matter. There was no free gold present. The solid was collected, and dissolved in 100 c.c. of water with the aid of 22 c.c. of saturated sodium hydrogen carbonate solution. Addition of 30 g. of sodium chloride caused the separation of a white, amorphous precipitate of the sodium salt of the crude aurothiol acid. It was redissolved in 100 c.c. of water, by gentle warming with addition of a few drops of 2*N*-sodium hydroxide, and reprecipitated by 30 g. of sodium chloride. This process was repeated in order to eliminate the last traces of thiol acid. The amorphous sodium salt was suspended in water and treated with excess of 3*N*-hydrochloric acid, and the

amorphous aurothiol acid was centrifuged off, resuspended in water, and re-centrifuged so long as the supernatant fluid showed chloridion. The acid, after being dried in a vacuum and ground, was obtained as a pale primrose-yellow powder (yield, 2·7 g. or 77%) (Found: Loss on prolonged drying at 110°, 6·3%. Found in anhydrous solid: N, 7·6; Au, 57·8, 57·8. $C_5H_5O_2N_2SAu$ requires N, 7·9; Au, 55·6%). On ignition even with nitric and sulphuric acids, this aurothiol acid leaves a residue of gold soluble in cold aqua regia but containing a small quantity of insoluble black material. This is destroyed by digestion with hot aqua regia, and after removal of nitric acid the gold can be quantitatively precipitated by excess of ferrous chloride in acid solution. If insufficient acid be added, the gold contains a large quantity of iron (compare Treadwell, "Analytische Chemie," 1921, II, 213).

The aurothiol acid forms a clear pale yellow solution on neutralisation with sodium hydrogen carbonate and can be boiled without decomposition.

The first two sodium chloride precipitation liquors of the sodium salt, on acidification to Congo-paper, gave precipitates of 1·37 g. and 0·1 g., respectively, of crystalline 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid. This was identical in all its reactions with the 2-thiol acid prepared by hydrolysis of its ethyl ester. In particular, 1·2 g. were esterified by alcoholic hydrogen chloride and gave 1·1 g. of ethyl 2-ethylthiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate.

In some experiments, the salting-out of the amorphous sodium salt of the aurothiol acid led to simultaneous separation of flattened needles of the sodium salt of the 2-thiol acid. This could be eliminated only by increasing the number of precipitations.

Action of Mercuric Acetate on Ethyl Glyoxaline-4(or 5)-*carboxylate*.—Ethyl glyoxalinecarboxylate (0·7 g.) was dissolved in 25 c.c. of alcohol and treated with 1·6 g. (1 mol.) of mercuric acetate. The gelatinous mass immediately produced was boiled for 6 hours; it then consisted of homogeneous, microscopic, flat prisms almost insoluble in cold alcohol (yield, 2·0 g.). *Ethyl* 1-*acetoxymercuri-glyoxaline*-4(5?)-*carboxylate* (IX) is instantly soluble in dilute hydrochloric acid, and black mercuric sulphide is precipitated from the solution by hydrogen sulphide. Sodium hydroxide produces orange-yellow mercuric oxide. The ester has no definite melting point, but shrinks suddenly at about 222° and is not further changed at 300° (Found: Loss at 100°, 2·8. $C_8H_{10}O_4N_2Hg,\frac{1}{2}H_2O$ requires H_2O, 2·2%. Found in dried substance: N, 6·8; Hg, 50·8. $C_8H_{10}O_4N_2Hg$ requires N, 7·0; Hg, 50·4%).

Action of Mercuric Chloride on Ethyl 2-*Thiol*-4(or 5)-*methyl-glyoxaline*-5(or 4)-*carboxylate*.—The thiol ester (1·86 g.) was boiled

with 5·4 g. (2 mols.) of mercuric chloride in 50 c.c. of absolute alcohol for 6 hours. On standing for a few days, *ethyl 2-chloromercurithiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate* (X), m. p. 167—168°, separated in six-sided plates (yield, 95%). It was soluble without difficulty in 3 volumes of boiling absolute alcohol (Found: N, 6·5. $C_7H_9O_2N_2ClSHg$ requires N, 6·7%). The ester does not give mercuric oxide on treatment with sodium hydroxide, but is immediately blackened by ammonium sulphide.

Action of Mercuric Chloride on 2-Thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic Acid.—The thiol acid (1·58 g.), dissolved in 100 c.c. of pure dry methyl alcohol, was boiled for 6 hours with 5·43 g. (2 mols.) of mercuric chloride. After remaining for 12 hours at room temperature, the solution deposited 0·25 g. of substance, and on concentration a further 0·8 g. *2-Chloromercurithiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid* (XI), m. p. 257° (efferv.), is readily soluble in sodium hydrogen carbonate solution and is precipitated unchanged, but microcrystalline, on addition of hydrochloric acid (Found: N, 7·1. $C_5H_5O_2N_2ClSHg$ requires N, 7·1%). Mercuric sulphide is readily precipitated when hydrogen sulphide is passed into a suspension of the acid in hot dilute mineral acid solution, or instantly by the action of ammonium sulphide. The acid does not give mercuric oxide on treatment with sodium hydroxide.

Action of Hydrogen Peroxide on 2-Thiol-4(or 5)-methylglyoxaline.—Finely powdered thiolmethylglyoxaline (1·14 g.) was added in portions to a stirred solution of 2·4 g. (2 mols.) of Merck's perhydrol in 6 c.c. of water at 0° to −5°. The thiol compound rapidly passed into solution through oxidation and yielded a clear solution which after a short time became filled with microscopic leaflets of *4(or 5)-methylglyoxaline-2-sulphinic acid* (XV). These were filtered off on an ice-jacketed funnel at 0° and washed with ice-cold water (yield, about 0·7 g.). For analysis, portions were removed, rubbed quickly on ice-cold porous plate, and rapidly weighed (Found: N, by Kjeldahl's method, 15·7; SO_2 evolved by digestion with boiling dilute sulphuric acid and absorbed by aspiration in *N*/10-iodine, 36·7; N in distillation residue, by Kjeldahl's method, 15·9—whence $SO_2 : N = 1·01 : 2$. $C_4H_6O_2N_2S,2H_2O$ requires SO_2, 35·2; N, 15·4%. Found: oxygen consumed by oxidation with *N*/10-permanganate in 2*N*-sulphuric acid at 0°, 8·1. $C_4H_6O_2N_2S,2H_2O$ requires O, 8·8%). This sulphinic acid is an unstable substance. When kept for a few hours either in a vacuum over sulphuric acid or in the air at room temperature, it passes into a clear basic liquid with loss of some sulphur dioxide. This liquid residue, when kept dry or when heated on the water-bath, partly crystallises as the normal *sulphite* of 4-methylglyoxaline. If the basic residue be

mixed with saturated potassium carbonate solution and extracted with chloroform, the latter on evaporation yields a base which readily crystallises completely as 4-methylglyoxaline. The sulphinic acid melts at 73° and effervesces at 92°. It is faintly acid to sensitive methyl-orange paper and dissolves in sodium hydrogen carbonate solution with evolution of carbon dioxide. It is not very readily soluble in ice-cold water and gives no precipitate with ferric chloride. Its ammoniacal solution gives no precipitate with calcium or barium chloride.

The mother-liquors of the oxidation were evaporated to a small volume over sulphuric acid in a desiccator and then deposited clusters of fine needles (0·1 g.) of the corresponding sulphonic acid (see below). The mother-liquor also contained sulphate and 4-methylglyoxaline, the latter being readily removed from saturated potassium carbonate solution by chloroform.

4(or 5)-*Methylglyoxaline-2-sulphonic Acid* (XVI).—2-Thiol-4(or 5)-methylglyoxaline (0·57 g.) was oxidised by hydrogen peroxide (3 mols.) in the way described in the previous section. When the sulphinic acid had crystallised from the liquor, 2*N*-sodium hydroxide (2 c.c.) was added drop by drop until an alkaline reaction was attained. The clear solution was concentrated at room temperature over sulphuric acid in a vacuum for 12 hours and had then become acid (decomposition of sulphinic acid) in reaction with deposition of a few crystals of the sulphonic acid. It was made acid to Congo-paper and gradually deposited the sulphonic acid (yield 0·55 g.). For analysis, 0·35 g. was dissolved in 0·2 c.c. of hot water and gave 0·3 g., crystallising in stout columns, m. p. about 280° (Found: Loss at 100°, 10·3. $C_4H_6O_3N_2S,H_2O$ requires H_2O, 10·0%. Found in dried substance: N, 16·9. $C_4H_6O_3N_2S$ requires N, 17·2%). This sulphonic acid is faintly acid to Congo-paper and methyl-orange paper and is stable to acid permanganate. The *calcium* and *barium* salts are very soluble in water. The *ammonium* salt is readily soluble, but crystallises well in microscopic rods.

Action of Sulphur Dioxide on 2-Thiolglyoxalines.—If 2-thiol-4(or 5)-methylglyoxaline, ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate or 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid be dissolved in *N*-hydrochloric acid and subjected to a current of sulphur dioxide, the solution immediately becomes yellow. The same behaviour is shown by thiocarbamide but not by cysteine. When 2-thiol-1-phenylglyoxaline, 2-thiol-1-phenyl-4-methylglyoxaline, 2-thiol-1 : 5-dimethylglyoxaline, and 2-thiol-1 : 4-dimethylglyoxaline are dissolved in water and saturated with sulphur dioxide, yellow solutions are produced and in the case of the two 1-phenyl derivatives orange-yellow crystalline addition

products separate readily. These are stable in presence of excess of sulphur dioxide, but redissolve as the sulphur dioxide passes off. 2-Thiol-4 : 5-diphenylglyoxaline, unlike all the other 2-thiolglyoxalines examined, showed no visible change, possibly owing to its sparing solubility in water. When sulphur dioxide is passed over powdered 2-thiolglyoxalines, they become yellow to orange-yellow through absorption of the gas. Thus 2-thiol-1-phenyl-, 2-thiol-1-phenyl-4-methyl-, 2-thiol-1 : 5-dimethyl-, 2-thiol-4-methyl-, and 5-carbethoxy-2-thiol-4-methyl-glyoxalines all become yellow on exposure to sulphur dioxide. Thiocarbamide became pale yellow, but 2-thiol-1 : 4-dimethylglyoxaline and allylthiocarbamide (thiosinamine) immediately liquefied on exposure to the gas, forming orange and yellow liquids respectively. 5-Carbethoxy-4-methyl-2-glyoxaline disulphide went deeper yellow on exposure to the gas and in aqueous suspension was rapidly reduced to the corresponding thiol compound. The hydrated form of ergothioneine from blood was immediately converted into an orange-coloured, pasty product by exposure to sulphur dioxide.

Quantitative Absorption Experiments.—Finely divided 2-thiol-1-phenylglyoxaline (0·0712 g.) was submitted to a current of sulphur dioxide in a small U-tube fitted with pierced ground glass stoppers and side arms. Absorption of the gas was rapid and at the end of 2 hours 0·0249 g. had been absorbed. From this point absorption was slow and after 12 hours the total absorption was 0·0263 g., corresponding to 1·01 molecule of sulphur dioxide. When this compound was exposed to the air in an open boat, it was one-half dissociated in 10 minutes. In a similar manner, thiocarbamide (0·1211 g.) absorbed 0·74 molecule of sulphur dioxide in 15 hours, becoming pale yellow; absorption thereafter was very slow. Korczyński and Glebocka (*loc. cit.*) found absorption of 0·5 mol. and described their product as white. In the former case, after the sulphur dioxide had completely gone, the m. p. of the original substance was unchanged. In the latter case, there was a slight depression. A control experiment on ethyl 4(or 5)-glyoxaline-carboxylate showed negligible absorption of sulphur dioxide.

Colour Reactions for Thiolglyoxalines.—The colour reactions of thiolglyoxalines with sulphur dioxide and with auric chloride have been described above. Sato's reaction for thiocarbamide (*loc. cit.*) is applicable to thiolglyoxalines and is best carried out as follows : The substance is dissolved in water, treated with one drop of glacial acetic acid followed by one drop of potassium ferrocyanide solution; a yellowish-green solution is then produced which on warming rapidly becomes intense blue. Tschugaev's reaction (*Ber.*, 1902, **35**, 2483) for thiocarbamide, an intense gentian-blue on warming

with benzophenonechloride, although given by allylthiocarbamide, is not given by 2-thiolglyoxalines. Rheinboldt's reaction for thiol groups (*Ber.*, 1927, **60**, 184)—a wine-red solution—does not apply to 2-thiolglyoxalines or thiocarbamides, which all give yellow solutions. Tanret (*Compt. rend.*, 1909, **149**, 222) described a colour reaction for ergothioneine, which, on warming with chloroform and potassium hydroxide solution, gave a green solution which became blue on acidification. This reaction has been tried on a wide variety of thiolglyoxalines, glyoxalines, and thiocarbamides and is not specific for the thiol group. Thiocarbamides give nothing distinctive and in the glyoxaline group the reaction is probably of value for the diagnosis of constitution. Whilst 2-thiol-4(or 5)-methylglyoxaline gives an eosin-red solution which on careful addition of acid becomes blue, other glyoxalines, when they do give a colour, generally give a yellow or orange-yellow solution which may or may not be discharged by acids. In some cases, the yellow colouring matter is soluble in chloroform. Thus 4(or 5)-methylglyoxaline gives a bright yellow solution, 2-thiol-1 : 4-dimethylglyoxaline gives a yellow solution, whilst its isomeride, 2-thiol-1 : 5-dimethylglyoxaline, gives no colour. Again, 2-thiol-1-phenylglyoxaline gives no colour, whereas 2-thiol-1-phenyl-4-methylglyoxaline gives a bright yellow colour in the aqueous and chloroform layers. The reaction seems to be conditioned by the presence of at least one substituent in the 4- or 5-position, but both may be substituted if carboxyl or carbethoxyl is one, as these probably suffer replacement. Finally, if the hydrogen attached to nitrogen is displaced, only the 1 : 4-disubstituted derivatives produce colour. The reaction is possibly dependent on the formation of the triglyoxaline analogues of the triphenylmethane dyes.

A reaction which appears to be new for thiocarbamides and 2-thiolglyoxalines is the intense blue colour produced when an ammoniacal solution of the substance to be tested is treated with a drop of phosphomolybdic acid. This reagent shows the great ease with which 4(or 5)-carbethoxy-5(or 4)-methyl-2-glyoxaline disulphide is hydrolysed with production of the thiol group by very brief boiling in ammoniacal solution.

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NATIONAL INSTITUTE FOR MEDICAL RESEARCH,
HAMPSTEAD.

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CCXLI.—*Chemical Action at an Interface: The Production of Acidity in Neutral Salt Solutions.*

By N. VENKATANARASIMHA ACHAR and FRANCIS L. USHER.

THE frequently noticed development of acidity in neutral salt solutions in the presence of material from which no detectable quantity of acid can be extracted by pure water can be accounted for by assuming (1) a simple chemical interaction between the salt and a definite acid or mixture of acids, (2) a preferential absorption of the base of the salt, or (3) an exchange between the kations of the salt and hydrogen ions previously adsorbed by the material (Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 191). The second explanation assumes the selective adsorption of hydroxyl ions from water, and can evidently be employed, alternatively with the third, to account for acidity produced by materials which are not regarded as actual or potential acids.

The first, or "chemical," theory has been objected to on the ground that, if the materials dealt with contain acids, the latter must be both insoluble, since the water extracts are neutral, and strong, in that they are able to decompose salts of the strong mineral acids; but no acids of this character are known. The purpose of this paper is to show that the effects observed with materials of complex and undetermined composition may also be observed with a simple insoluble weak acid; that these effects may properly be regarded as arising from an ordinary chemical interaction of the ionic type, qualified by the circumstance that one of the ions is non-diffusible; and that their occurrence is a logical consequence of the "surface dissociation" theory. This theory was developed by Pauli in connexion with colloidal suspensions, and advocated by McBain in the case of electrokinetic phenomena, and it does not require the assumption of selective adsorption.

If the molecules in the surface of an insoluble acid in contact with water are imagined to undergo dissociation, and if the hydrogen ions so produced are osmotically active and have a range of movement determined by the electrostatic field due to the residual acid anions on the surface, such a system is separated from the external liquid by an imaginary envelope which marks the extreme range of movement of the hydrogen ions, and is equivalent to a membrane permeable by any ions except the acid anions embedded in the surface of the insoluble acid. When the external liquid is pure water, this, on separation from the insoluble acid, should not have acquired hydrogen ions from the latter, since they are electrostatically tethered to its surface; but if a neutral salt is present in the water,

an exchange should take place between some of the hydrogen ions within the envelope and an electrically equivalent number of kations in the external liquid. On the foregoing assumptions, a solution of a neutral salt in contact with, *e.g.*, stearic acid, should become acid, and the total acid present should increase with increase of the volume of solution per unit surface of the solid, in consequence of the progressive dissociation of the molecules in the surface; or alternatively, if this ratio is kept constant, the acidity should vary directly with the concentration of the salt within the limits denoted by the principle of "membrane equilibrium." The experiments with stearic acid described below confirm these expectations, and suggest an equally simple explanation of the results obtained by Mukherjee and his co-workers (J., 1926, 3023) in the case of hydrated silica.

EXPERIMENTAL.

Some experiments were carried out with colloidal suspensions of stearic acid in water, in order to ascertain the order of magnitude of the acidity, if any, produced in neutral solutions of potassium chloride. The stearic acid used (Kahlbaum's best) was recrystallised twice from neutral methyl alcohol. It was shown that this degree of purification furnished a material the solubility of which in water ($3{\cdot}5 \times 10^{-6}$ equiv. per litre) was not further reduced by repeated recrystallisation (compare Bowden, J., 1911, **99**, 192; Bunbury and Martin, J., 1914, **105**, 418). The acid was dispersed by dropping a dilute methyl-alcoholic solution into boiling "conductivity" water contained in a large Jena-glass flask, the methyl alcohol being removed by continued boiling. To 50 c.c. of this suspension 25 c.c. of a neutral solution of potassium chloride were added, and the mixture was either filtered through an "ashless" filter, or, if coagulation was incomplete, submitted to ultrafiltration through a collodion membrane, the first portions of the filtrate being rejected. 10 C.c. of the clear liquid were then titrated against standard sodium hydroxide, and the acidity was calculated after the value obtained by titrating the ultrafiltrate from a suspension in water alone had been subtracted. The last-named ultrafiltrate was considered to be a saturated solution of stearic acid in water, but the solubility as determined from it is probably slightly in excess of the true value, because the liquid, in spite of its apparent clarity, may have contained a few ultramicronic and amicronic particles. The true values of the acidity due to the salt action should probably therefore be rather higher than those in Table I. It is also to be observed that, although atmospheric carbon dioxide was not rigidly excluded, the solubility determination itself constituted a control

experiment, so that any error due to this cause can only be a difference between two small and nearly equal errors.

The liquids, excepting the alkali contained in the microburette, were handled in vessels coated with hard, neutral paraffin wax, and the experiments were carried out at the ordinary temperature (about 23°). The results are in Table I.

TABLE I.

50 c.c. Stearic acid suspension + 25 c.c. KCl solution.

Normality of KCl in mixture ...	0·001	0·007	0·027	0·083	0·33	0·84
Normality ($\times 10^6$) of acid due to salt action	6	7	16	26	32	49

A second series of experiments had for its object the accurate determination at the ordinary temperature of the relation between acidity and salt concentration, and between acidity and the volume of salt solution per unit surface of stearic acid. The method used was the electrical measurement of the hydrogen-ion activity of mixtures of stearic acid suspensions with neutral solutions of potassium sulphate. The hydrogen-ion activity of solutions of potassium sulphate at the three dilutions employed, when containing various known quantities of sulphuric acid, was also measured separately, and curves were drawn from which the actual quantity of sulphuric acid liberated by the suspensions could be read off. Preliminary experiments with an ordinary hydrogen electrode were discontinued on account of the unsatisfactory readings obtained, due possibly to the spoiling of the platinised surface of the electrode by particles of stearic acid. A bright platinum quinhydrone electrode gave satisfactory and reproducible results.

The quinhydrone, stearic acid, and potassium sulphate were recrystallised several times, the best-quality " conductivity " water was used, and no liquid of which the hydrogen-ion activity was to be measured was ever in contact with glass other than well-steamed Jena-glass or glass coated with neutral, hard paraffin wax. The liquid was deprived of dissolved carbon dioxide, before measurements were made, by prolonged passage of carbon dioxide-free air saturated with the vapour of the liquid under examination. A " saturated " calomel electrode was used as the second pole of the combination the *E.M.F.* of which was measured, and the combination was kept on an earthed metal sheet in a large air thermostat at 29° (the room temperature during these experiments being usually 27—28°). In order to avoid contact of the liquids with soda-glass measuring vessels, the solutions were prepared in every case by weight, not volume. The solutions of known acidity were made up by adding sulphuric acid of known strength contained in a paraffined

weight-pipette to 25 g. of potassium sulphate solution of double the strength required, in a tared Jena-glass flask, the final weight being then made up to 50 g. with conductivity water. The stearic acid mixtures contained equal weights of the suspension and of the potassium sulphate solution. If coagulation occurred before dissolved carbon dioxide was removed, as it did with the $N/2$-salt solutions at all dilutions except the highest, the liquid was filtered through an " ashless " paper, and the first 10 c.c. were rejected. If coagulation occurred either not at all or only after the bubbling of air, the unfiltered liquid was used. The relative hydrogen-ion activities were calculated from the formula $\log f = (E - 0{\cdot}4536)/0{\cdot}0598$, in which E denotes the measured $E.M.F.$ of the combination. The values of the hydrogen-ion activities corresponding to various concentrations of sulphuric acid in the three solutions of potassium sulphate used are in Table II. The figures are calculated on the assumption that the potential at the K_2SO_4-saturated KCl junction is zero, an assumption which does not affect their validity for the purposes of this investigation.

TABLE II.

	$N/100$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	26·80	6·77	4·97	2·02			
Relative $H^{\cdot}$ activity ($\times 10^6$)	15·45	4·45	3·57	1·62			
	$N/10$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	55·8	28·0	20·07	14·55	6·89	4·64	2·72
Relative $H^{\cdot}$ activity ($\times 10^6$)	17·42	8·38	6·72	4·58	2·47	1·73	1·19
	$N/2$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	269	145	52·8	33·66	20·79	13·06	5·94
Relative $H^{\cdot}$ activity ($\times 10^6$)	39·84	21·52	6·78	3·88	2·26	1·57	1·10

Table III gives the results of the measurements of acidity produced by the stearic acid suspensions. The figures headed " dilution " refer to dilutions of the stock suspension which contained 2·32 g. of stearic acid per litre. Columns A, B, and C contain, respectively, the relative hydrogen-ion activities ($\times 10^6$), the concentration of acid (g.-equivs. $\times 10^6$ per kg.), and the total acid liberated (g.-equivs. $\times 10^6$ per g. of stearic acid). The figures are calculated from the mean of two or more separate measurements in each case.

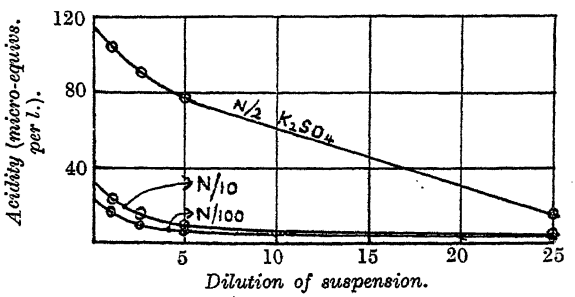
TABLE III.

	Normality of K_2SO_4 solution.								
	$N/100$.			$N/10$.			$N/2$.		
Dilution.	A.	B.	C.	A.	B.	C.	A.	B.	C.
1	10·4	16·2	13·9	7·75	23·3	20·1	15·4	105	90·6
2·5	6·52	8·8	18·9	5·14	14·8	31·9	12·8	91·5	197
5	4·98	6·0	25·8	3·35	8·5	36·6	10·6	77·6	333
25	3·88	4·14	89·6	2·12	4·4	94·8	1·98	15·8	340

The Nature of the Reaction between an Insoluble Acid and Salt Solutions.

The application of the theory of " membrane equilibrium " to the present problem is complicated by two factors which were not included in the theory as originally formulated by Donnan, *viz.*, (1) the unknown ratio of the volumes of liquid on either side of the " membrane," and (2) incomplete dissociation of the non-diffusible substance, involving the possibility of an increase in the number of diffusible ions available for exchange. In the absence of any knowledge of the magnitude of these factors, no quantitative application of the theory is possible; but an examination of the results of the experiments just described is strongly in favour of the conclusion that the reaction under discussion (and, by implication, similar reactions in which acidity is produced in neutral salt solutions) is qualitatively accounted for by the theory.

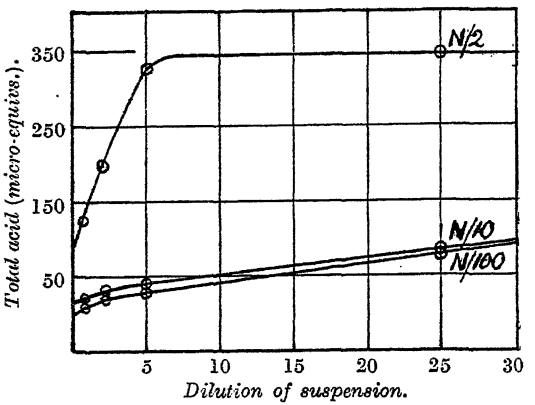
FIG. 1.



The progressive dilution of a suspension by the salt solution used is equivalent to increasing the volume of the liquid containing only diffusible ions, while maintaining constant that of the liquid containing the non-diffusible ion. If no dissociation of the surface molecules of the insoluble acid takes place, the activity of the hydrogen ions in the external liquid should decrease in an approximately linear manner with the dilution, provided that the volume of the external liquid is always a large fraction of the total volume, as it almost certainly is when the suspension is dilute. Assuming, on the other hand, that the surface molecules are initially but slightly dissociated, then if there were an unlimited supply of such molecules, which could undergo progressive dissociation, the hydrogen-ion activity in the external liquid should show little change with dilution. Under the experimental conditions the supply of surface molecules is limited, and it can be seen from Fig. 1 that, at the higher dilutions, the observations nearly correspond to these two extreme cases. Since a concentrated salt solution produces a more complete

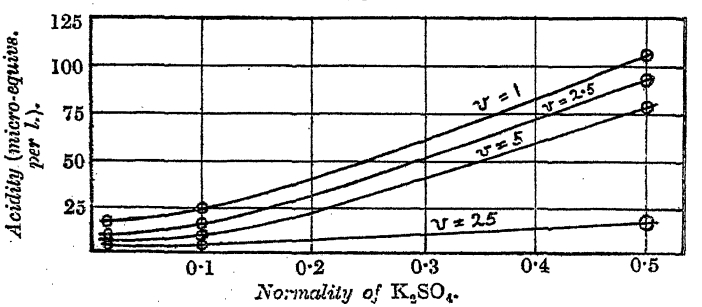
exchange of ions than do the more dilute solutions, the reserve of undissociated molecules is in the former case nearly exhausted initially, and very little further dissociation is possible as the volume is increased; on the other hand, in the dilute solutions the acid concentration is comparatively little affected by dilution. Fig. 2,

FIG. 2.



showing the relation between dilution and total acid liberated, provides a striking clue to this behaviour: practically all the available acid is liberated by the strong salt solution during the early part of the dilution process (1 to 5), and further dilution (5 to 25)

FIG. 3.



produces no more. With the weaker solutions, the production of acid is still in evidence even at the highest dilution.

Again, the increase of acidity due to an increase in the concentration of potassium sulphate (see Fig. 3) is, at least qualitatively, predicted by the theory of membrane equilibrium. The increase is considerably greater than would be expected in a system where the number of exchangeable ions is constant, and this constitutes

additional evidence of the dissociation of the surface molecules under the experimental conditions.

The Relation between Acid Concentration and Hydrogen-ion Activity.

Donnan's theory is concerned with activities rather than concentrations, but in the present experiments the activity relationships tend to be obscured by disturbing factors incidental to the method used. In the presence of an excess of potassium sulphate, any sulphuric acid liberated is present as potassium hydrogen sulphate which, itself a strong binary electrolyte, furnishes an anion which is an acid with a dissociation constant of about 10^{-2} (Drucker, *Z. physikal. Chem.*, 1920, **96**, 382). An increase in the concentration of potassium sulphate may therefore be expected to influence the hydrogen-ion activity and the acid concentration in opposite senses, because a higher concentration of the salt, whilst effecting a more complete exchange of hydrogen ions, will at the same time cause a greater proportion of them to assume an inactive condition. This is, in fact, observed, for the activity–salt concentration curves pass through a minimum except at the highest dilution of the suspension.

Although it is chiefly a matter of terminology whether the production of acid, in circumstances similar to those considered in this paper, is to be regarded as an ionic exchange or as a chemical reaction between equivalent quantities of two molecular species, the suggestion has been put forward (Mukherjee, *loc. cit.*), in the case of hydrated silica, that the production of acid is to be attributed to an exchange of *adsorbed* ions bearing no stoicheiometric relation to the number of molecules of silica associated with them. The point of view advocated here differs radically from Mukherjee's in regarding the action as taking place between quantities of the insoluble acid and the neutral salt which are in a simple stoicheiometric proportion; in other words, one is dealing with a reversible chemical change differing from the ordinary type only in its localisation at an interface. The advantages of this point of view are that it does not need to invoke any of the various types of adsorption, and is at once in harmony with accepted chemical theory and with a theory of interfacial behaviour for which there is a rapidly increasing body of evidence (see *Trans. Faraday Soc.*, 1925, **21**, 406).

Summary.

1. The production of acidity by suspensions of stearic acid has been measured in neutral solutions of potassium chloride and potassium sulphate.

2. The variation of hydrogen-ion activity and of total acid with the salt concentration and with dilution of the suspension has been

examined, and found to be consistent with the view that the observed acidity is produced by exchange of the kations of the salt with hydrogen ions formed from dissociating molecules in the surface of the insoluble acid.

3. It is considered that the production of acidity in neutral solutions of salts of strong acids in contact with an extensive surface of a weak insoluble acid is generally to be expected on the basis of accepted theory, and is capable of a simple chemical interpretation.

UNIVERSITY OF MYSORE,
BANGALORE.

THE UNIVERSITY, LEEDS.
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CCXLII.—*Reactions of Incandescent Tungsten with Nitrogen and with Water Vapour.*

By COLIN JAMES SMITHELLS and HAROLD PERCY ROOKSBY.

(COMMUNICATION FROM THE RESEARCH STAFF OF THE GENERAL ELECTRIC COMPANY, LTD., WEMBLEY.)

1. *Reaction with Nitrogen.*

THE temperature at which a tungsten filament can be operated in a vacuum is in practice limited by the rate of evaporation of the metal, which forms a black deposit on the bulb, thereby reducing the candle power of the lamp. By surrounding the filament with an atmosphere of inert gas, the loss of metal by evaporation is reduced, and the filament can be operated at a higher temperature, and therefore at a higher efficiency, for an equal life (Brit. Pat., 10,918, 1913). In lamps of small wattage, it is customary to use as the inert gas a mixture of argon and nitrogen containing 10—20% of the latter, but lamps of 500 watts and upwards are frequently filled with pure nitrogen on grounds of economy. The filaments operate at a temperature of about 2850° K. It is found that a dark brown deposit is slowly formed on the inside of the bulb during the life of such lamps; but it forms much more slowly if an argon–nitrogen mixture is used. The cause of this coloration has now been investigated.

Very little information exists as to the formation, composition, or properties of the nitrides of tungsten. Henderson and Galletly (*J. Soc. Chem. Ind.*, 1908, **27**, 387) heated tungsten powder to 860° in a current of ammonia, but the product contained only a trace of nitrogen. By heating "tungsten nitramide," $W_3N_6H_4$, in ammonia, Uhrlaub ("Die Verbindungen einiger Metalle mit Stickstoff," Göttingen, 1859) obtained a substance to which he

assigned the formula W_3N_2. By heating tungsten hexachloride in ammonia, Rideal (J., 1889, **55**, 41) obtained a black, metallic-looking powder, the composition of which was represented as W_2N_3.

Langmuir (*J. Amer. Chem. Soc.*, 1913, **35**, 931) has studied the rate at which nitrogen is absorbed in a tungsten-filament vacuum lamp. He found that this was dependent on the rate of evaporation of the filament, and that one molecule of nitrogen disappeared for each atom of tungsten evaporated. He therefore assumed that nitrogen did not react with solid tungsten at temperatures in the neighbourhood of 2200° K., but that when an atom of tungsten struck a molecule of nitrogen they combined to form WN_2, which was deposited on the bulb. This nitride is described as a brown compound, readily decomposed by water to form ammonia and tungstic oxide, WO_3. No direct analyses were made.

It appeared probable that the coloration of the lamps under consideration might be due to the formation of such a nitride. Alternatively, it was possible that the deposit was evaporated tungsten from the filament, or nickel or molybdenum from the supporting and leading-in wires. The presence of traces of oxidising gases might also give rise to oxides of any of these metals. The total weight of the deposit on the inside of the largest lamps, which have a capacity of about 4 litres, is only 5—10 mg. after the lamp has been operated for 1000 hours. Special methods of analysis had, therefore, to be developed.

Preliminary Examination.—On opening the lamp a distinct odour is observed, which resembles ammonia, but is difficult to identify. The deposit can easily be rubbed off with the finger, or scraped together with a knife. After being exposed to the air for an hour, it becomes slightly sticky, more difficult to remove, and somewhat lighter in colour. After two or three days' exposure, it is again quite dry and easily rubbed off. A small quantity was ignited in air and gave a greenish-yellow residue, which resembled tungstic oxide and yielded its characteristic *X*-ray pattern, thus proving that the original material was definitely tungsten or one of its compounds.

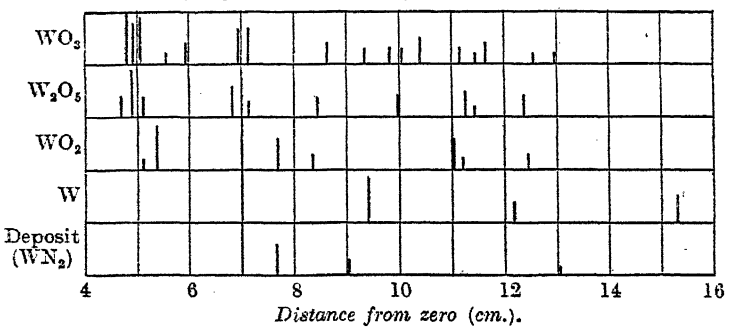
X-Ray Examination.—Tungsten forms three oxides, which are readily distinguished by their colour: WO_3, yellow; W_2O_5, deep blue; and WO_2, chocolate-brown. Pure specimens of each of these oxides were prepared, and the characteristic *X*-ray diffraction patterns obtained, together with that of the metal. These are shown in Fig. 1, where the height of the lines represents their relative intensities on the film. A little of the deposit was then smeared on a piece of tissue paper, and exposed to the *X*-ray beam. Three strongly marked but somewhat diffuse lines appeared in the

pattern. Although they were sufficiently clear for purposes of identification, it was not easy to measure their position accurately. The diffuseness was due to the extremely fine state of division of the deposit. By heating another sample at 600° in a current of pure, dry argon for 2 hours, the particles became coarser, and the lines in the diffraction pattern appeared much sharper. Their position, however, was unchanged. This pattern is also shown in Fig. 1. On comparing the positions of the lines with those in the patterns of the metal and its oxides, it is clear there is no correspondence and that the deposit must be some other compound.

Spectroscopic Examination.—The fact that the material burnt readily in air to tungstic oxide suggested a simple way of proving whether it was a nitride, for nitrogen should be formed when such a compound is oxidised.

FIG. 1.

X-Ray diffraction patterns of tungsten compounds.

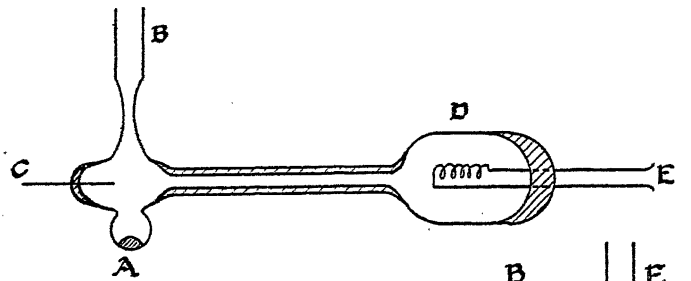


A small hard-glass spectrum tube was made as shown in Fig. 2. This had a bulb, A, into which a mixture of the deposit with a little potassium permanganate was introduced through B. A plain molybdenum electrode, C, was arranged at this end, whilst at the other end of the tube a thick tungsten spiral filament, D, acted as the second electrode for the discharge. The electrodes were thoroughly freed from gas before the mixture was introduced, after which the tube was evacuated and sealed off. The whole volume of the apparatus was less than 1 c.c., and since a pressure of about 1 cm. was sufficient to obtain a satisfactory discharge, only 0·0003 g. of material was necessary.

On heating the bulb, A, a vigorous reaction occurred between the material and the permanganate. On passing a discharge, the spectrum of both nitrogen and oxygen appeared. The excess oxygen, derived from the permanganate, was then removed by heating the tungsten filament, and finally the tube contained nearly

pure nitrogen. The material was therefore most probably a nitride of tungsten having the formula WN_x.

FIG. 2.
Discharge tube.



Composition of the Nitride.—The value of x was determined by measuring (*a*) the volume of oxygen required to burn a small weight of the material, and (*b*) the volume of nitrogen evolved. From the equation

$$2WN_x + 3O_2 = 2WO_3 + xN_2,$$

it is seen that the value of x is determined from the ratio of the volumes of oxygen and nitrogen. It is not necessary to know the weight of the nitride, but, as a further check on the analysis, the material was weighed before the combustion was carried out. A special form of combustion apparatus was made (Fig. 3) which consisted of a hard-glass tube, A (volume about 3 c.c.), attached to a tap, B, and to a piece of barometer tubing, C (volume 1·5 c.c.). The lower end of the barometer tube was connected by a flexible rubber tube to a second piece of barometer tubing, D. The volume of the apparatus was carefully calibrated and a scale was attached to the tube C.

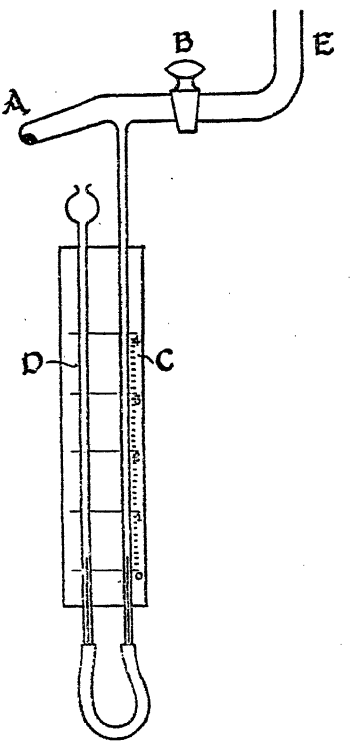


FIG. 3.
Combustion apparatus.

A weighed quantity (2—3 mg.) of the nitride was introduced into the limb A. The barometer U was filled with mercury up to about

the scale zero, and the tap closed. The whole apparatus was carefully protected from draughts and allowed to attain a steady temperature, which was read on an attached thermometer. The pressure was adjusted and the scale reading gave the volume of air in the apparatus. The nitride was then heated to about 650° by means of a blow pipe; it burnt readily to the yellow oxide, WO_3, and nitrogen was liberated. The apparatus was allowed to cool to room temperature during 5—10 hours, the pressure was adjusted, and the new volume read off. The difference between this reading and the previous one, after correction for any change of temperature, gave the volume of oxygen absorbed minus the volume of nitrogen evolved.

The external limb, E, was now filled with an alkaline solution of pyrogallol and the apparatus tilted so that when the liquid was drawn into the wide limb it would not enter the barometer tube. By lowering or raising the tube D, the solution was alternately drawn into the apparatus and expelled. The walls of the tube A were thus repeatedly wetted with fresh liquid until the remaining oxygen was absorbed. After allowing the apparatus to attain a steady temperature, a new reading of the volume was taken. This represented the known volume of nitrogen originally in the apparatus plus the nitrogen evolved.

The apparatus had been originally filled with atmospheric air, the humidity of which was determined from wet and dry bulb thermometer readings. It was found that the water-vapour pressure was, within the limits of accuracy attainable in the experiments, the same as that of the 40% caustic soda solution used for the absorption. No correction for the vapour pressure of the liquid was therefore required.

Although the formation of oxides of nitrogen during the combustion did not seem probable, caustic potash was introduced into the apparatus before the pyrogallol solution in one experiment. No absorption occurred, thus indicating that no oxides higher than nitrous oxide were present. It was thought justifiable to neglect the possibility of the presence of the latter.

From the equation we have

$$x/3 = \text{Vol. of } N_2 \text{ evolved/Vol. of } O_2 \text{ absorbed.}$$

Let c be the volume of nitrogen evolved and b the contraction on burning. Then

$$b = \text{Vol. of oxygen} - c,$$

and

$$x = 3c/(b + c).$$

After a number of preliminary trials to test the apparatus, two accurate determinations were made with weighed quantities of

materials from two different lamps. The results are given in Table I.

TABLE I.

Expt.	Weight of material (g.).	*b* (c.c.).	*c* (c.c.).	*x*.
1	0·0026	0·10	0·19	1·96
2	0·0036	0·15	0·27	1·93

These values show very good agreement and indicate that the nitride has the formula WN_2. Assuming this to be correct, it is possible to check the values obtained for *c* from the weight of material used. In both cases, the experimental value is about 70% of the theoretical value for the volume of the combined nitrogen. The difference is probably accounted for by the presence in the material of small fragments of glass and mica, with which it becomes unavoidably contaminated when the lamp is broken open.

These results confirm the conclusion reached by Langmuir as to the composition of the nitride, by an entirely different method. The formulæ assigned by earlier workers are probably in error owing to the difficulty of separating the nitride from the metal powder, and to the inherent difficulties of gravimetric methods when dealing with oxides and nitrides of tungsten, the molecular weights of which are so nearly the same.

The approximate density of the nitride was determined by weighing samples of 5—10 mg. in air and in benzene. A small pellet of the material was pressed in a steel die, and weighed in a pan made from aluminium foil which weighed only 8 mg. The pan holding the pellet was immersed in benzene in an evacuated vessel, in order to remove any occluded air, and its weight in the liquid then determined. The method was checked by determining the density of a pellet made from a thin film of tungstic oxide condensed on a glass surface; this gave a value of 6·3 g. per c.c., the density of fused crystalline tungstic oxide being 7·2 g. per c.c. Two determinations of the density of the nitride gave a mean value of 5 g. per c.c., with a maximum error of $\pm 0{\cdot}5$ unit.

2. *Reaction with Water Vapour.*

The action of water vapour on an incandescent tungsten filament has been described previously by one of us (Smithells, *Trans. Faraday Soc.*, 1921, **17**, 485). It was shown that a reversible reaction took place in which tungsten was oxidised at the hotter parts of the filament, and the oxide reduced to metal at lower temperatures and deposited on the cooler parts of the filament: $W + 2H_2O \rightleftharpoons WO_2 + 2H_2$. The reaction is accompanied by a

gradual blackening of the bulb, and it would be expected that this is due to a certain amount of both metal and oxide being carried by convection in the gas. Langmuir (*Gen. Electric Rev.*, 1926, **29**, 153) has shown, however, that atomic hydrogen, which is formed when molecular hydrogen comes in contact with incandescent tungsten, will reduce tungsten oxides at room temperature. It therefore appeared of interest to determine the nature of the deposit, which is nearly black and easily distinguishable from the nitride just described. The *X*-ray diffraction pattern was found to be identical with that obtained from pure tungsten powder, no trace of oxide being present. This can only be explained by assuming that atomic hydrogen formed during the reaction, and in contact with the incandescent filament, arrives at the surface of the glass and reduces any oxide deposited. That oxide molecules do reach the glass walls is almost certain, since the cyclic action can hardly be so complete as to prevent their escape entirely. The fact that they are subsequently reduced explains why even very minute quantities of water vapour have such a deleterious effect in gas-filled lamps. Water vapour present in the filling gas to the extent of 1 part in 10,000 parts will cause the filament to burn out in less than an hour.

GENERAL ELECTRIC COMPANY, LTD.,
WEMBLEY. [*Received, February 22nd*, 1927.]

CCXLIII.—*The Intermolecular Condensation of Styryl Methyl Ketones. Part I.*

By ROBERT DICKINSON, ISIDOR MORRIS HEILBRON, and FRANCIS IRVING.

IN a previous investigation (Dickinson and Heilbron, this vol., p. 14), 3 : 4-dimethoxystyryl methyl ketone was required. Apparently three different substances, m. p.'s 168° (Francesconi and Cusmano, *Gazzetta*, 1908, **38**, ii, 70), 85—86°, and 91—92° (Ryan and Plunkett, *Proc. Roy. Irish Acad.*, 1916, **32**, *B*, 199; Kaufmann and Radosević, *Ber.*, 1916, **49**, 675), are recorded in the literature under this name, all having been prepared by the alkali condensation of veratraldehyde with acetone.

We have now investigated these compounds in detail. The second and the third are undoubtedly identical, the true melting point being 86°. This compound is definitely 3 : 4-dimethoxystyryl methyl ketone, for (1) its molecular weight, determined

ebullioscopically, is normal; (2) in the presence of hydrogen chloride, it condenses with 2-naphthol-1-aldehyde, giving 3-3′ : 4′-dimethoxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron, *loc. cit.*); (3) it may be prepared by the methylation of 3-methoxy-4-hydroxystyryl methyl ketone; (4) it absorbs one molecule of bromine (the dibromide, however, could not be isolated); and (5) it readily condenses with veratraldehyde, in the presence of alkali, giving 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone, identical with the product obtained by Stobbe and Haertel (*Annalen*, 1909, **370**, 104), the constitution of which we have now confirmed by the preparation of its tetrabromide. Guimbal (*Dipl. et Sup.*, No. 212, Paris, 1921; compare Faillebin, *Ann. Chim.*, 1925, **4**, 445) has come to the same conclusion, but only on the results of analysis and cryoscopy; he records 84° as the melting point. Lapworth and Wykes (J., 1917, **111**, 790) also must certainly have had this same ketone in their hands, as was shown by the ease with which it was oxidised to dimethylcaffeic acid. They do not, however, give the method of preparation, or record the melting point of their product, but only refer to Francesconi and Cusmano (*loc. cit.*), whose product is entirely different and cannot yield dimethylcaffeic acid.

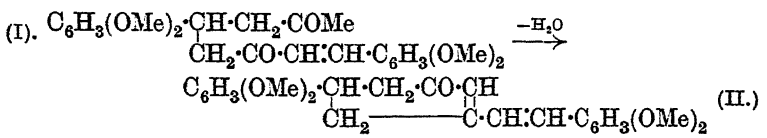
The compound described by Francesconi and Cusmano (*loc. cit.*) has also been obtained by other workers, who, beyond stating that it is not veratrylideneacetone and making suggestions as to its possible constitution, have not investigated it experimentally. It is regarded by Ryan and Plunkett (*loc. cit.*) as an isomeric form of the styryl ketone, by Kaufmann and Radosević (*loc. cit.*) as the corresponding distyryl ketone, and by Guimbal (*loc. cit.*) as a compound of 3 : 4-dimethoxystyryl methyl ketone and acetone. Francesconi and Cusmano (*loc. cit.*) do not record any analytical values for their compound, or for its alleged condensation product with cinnamaldehyde.

We have now found that in addition to its direct preparation from veratraldehyde and acetone, the 168°-compound may be obtained by treating 3 : 4-dimethoxystyryl methyl ketone with alkali, acetone being used as solvent in order to minimise the production of the distyryl ketone through scission (compare Heilbron and Buck, J., 1921, **119**, 1503). Our analyses show that the substance is formed according to the equations:

(A) $2C_6H_3(OMe)_2\cdot CHO + 2Me_2CO = C_{24}H_{26}O_5 + 3H_2O$
(B) $2C_6H_3(OMe)_2\cdot CH{:}CH\cdot CO\cdot CH_3 = C_{24}H_{26}O_5 + H_2O.$

From a knowledge of the addition reactions of unsaturated ketones, the first stage in equation (B) is undoubtedly represented by form-

ation of the compound (I) through simple addition at the αβ-ethenoid linkage.



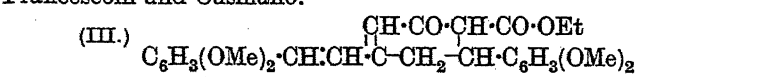
(I.) $C_6H_3(OMe)_2\cdot CH(CH_2\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)_2)\cdot CH_2\cdot COMe \xrightarrow{-H_2O}$ $C_6H_3(OMe)_2\cdot CH(CH_2\cdot CO\cdot C(CH_2)=C\cdot CH{:}CH\cdot C_6H_3(OMe)_2)$ (II.)

Many examples of such addition reactions are known; *e.g.*, Cornelson and Kostanecki (*Ber.*, 1896, **29**, 240) treated a mixture of 2-hydroxystyryl phenyl ketone and acetophenone with alkali and obtained 2-hydroxybenzylidenediacetophenone:

$$OH\cdot C_6H_4\cdot CH{:}CH\cdot COPh \xrightarrow{CH_3\cdot COPh} OH\cdot C_6H_4\cdot CH(CH_2\cdot COPh)_2.$$

Styryl and distyryl ketones add on acetoacetic ester and other keto-esters in precisely the same way, although secondary reactions occur afterwards (compare Heilbron and co-workers, J., 1924, **125**, 340, 2064; 1925, **127**, 2159; this vol., p. 918). The second stage of reaction (B) consists in the elimination of a molecule of water from compound (I), and this would almost certainly occur in such a manner as to yield the *cyclo*hexenone derivative (II).

The reactions of the 168°-compound are in full agreement with this formulation. We have determined its molecular weight, which is normal, and prepared its semicarbazone. It readily absorbs two molecules of bromine with exhibition of halochromy, but we have been unable to isolate the tetrabromide in a state of purity. Finally, full confirmation of formula (II) has been reached by the synthesis of the compound in the following way. 3 : 3′ : 4 : 4′-Tetramethoxydistyryl ketone was condensed with acetoacetic ester by means of sodium ethoxide (compare Heilbron and co-workers, *loc. cit.*); *ethyl* 3-mp-*dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (III) was then readily obtained in good yield. On treatment of this with 20% sulphuric acid, the carbethoxyl was eliminated with production of the free *cyclo*hexenone (II), which was identical in all respects with the compound described by Francesconi and Cusmano.



(III.) $C_6H_3(OMe)_2\cdot CH{:}CH\cdot C(CH\cdot CO\cdot CH\cdot CO\cdot OEt)=CH_2\cdot CH\cdot C_6H_3(OMe)_2$

We have attempted to obtain by similar means compounds analogous to (II), and for this purpose we prepared the *ethyl*, n-*propyl*, iso*propyl*, and *benzyl* ethers of 3-methoxy-4-hydroxystyryl methyl ketone. On treating these with alkali, we obtained the homologue of (II) in only one case—the *n*-propyl compound—and its reactions are in harmony with such a structure. An abnormal result was obtained with 3-*methoxy*-4-*benzyloxystyryl methyl ketone*,

treatment with alkali yielding a new substance (m. p. 174—175°) which gave analytical results for 3 : 3′-dimethoxy-4 : 4′-dibenzyloxydistyryl ketone, but was different from the distyryl ketone prepared in the usual manner (m. p. 155°). In all cases, much resinous material was formed; apparently the inter-condensation of styryl methyl ketones does not stop at the stage represented by equation (B), but continues to give a mixture of still more complex products. Such resinification of unsaturated ketones has already been considered by Borsche (*Ber.*, 1909, **42**, 4499), Giua (*Gazzetta*, 1925, **55**, 567), and especially by Herzog (*Z. angew. Chem.*, 1922, **35**, 465, 641; 1923, **36**, 471; *Chem.-Ztg.*, 1925, **49**, 119).

We next directed our attention to the action of piperidine upon styryl methyl ketones, expecting that this base would behave similarly to alkali, but would be milder in its action and possibly yield the primary additive compound (I). In all the cases we have investigated, however, much resinification took place, and we have been able to isolate solid products only in minute yields. These compounds are not true intermolecular condensation products, but dimerides of the styryl ketone, and from their saturated nature and absence of colour they must be regarded as *cyclo*butane derivatives (IV or V) analogous to that obtained by Stobbe (*J. pr. Chem.*, 1912, **86**, 248; Stobbe and Hensel, *Ber.*, 1926, **59**, 2254)

(IV.) $\begin{matrix} R\cdot CH\cdot CH\cdot COMe \\ R\cdot CH\cdot CH\cdot COMe \end{matrix}$ $\qquad$ $\begin{matrix} R\cdot CH\cdot CH\cdot COMe \\ COMe\cdot CH\cdot CHR \end{matrix}$ (V.) $\qquad [R = C_6H_3(OMe)_2]$

from phenyl 4-methoxystyryl ketone by the same method, and also to the compounds he and other workers have obtained by photopolymerisation (compare Stobbe and Hensel, *loc. cit.*).

Wieland (*Ber.*, 1904, **37**, 1145) obtained a dimeric form of phenyl styryl ketone by treating it with acetic anhydride containing a trace of sulphuric acid; but, applied to our compounds, this method yielded resinous material only, from which no pure substance has been isolated.

Experimental.

3 : 4-Dimethoxystyryl methyl ketone was prepared by Kaufmann and Radosević's method (*loc. cit.*) and found to melt at 85—86°, as given by Ryan and Plunkett (*loc. cit.*). The ketone can also be obtained in quantitative yield by the methylation of 3-methoxy-4-hydroxystyryl methyl ketone by Dickinson's method (J., 1926, 2234) for the preparation of 2-methoxystyryl benzyl ketone (Found: *M*,* 234, 207, 203. $C_{12}H_{14}O_3$ requires *M*, 206).

* The molecular weights recorded in this paper were all determined ebullioscopically in chloroform by Menzies's method (Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2314).

The *semicarbazone*, prepared by the usual method, crystallises from alcohol in colourless needles, m. p. 205°, which exhibit phototropic properties, becoming sulphur-yellow on short exposure to light. Crystallised from 50% acetic acid, it forms canary-yellow needles melting indefinitely about 180°. This is probably an unstable acetate, for on treatment with water or on keeping over potash it loses its crystalline form and colour, becoming identical with the original semicarbazone (Found: N, 16·1. $C_{13}H_{17}O_3N_3$ requires N, 16·0%).

3 : 3′ : 4 : 4′-Tetramethoxydistyryl ketone was obtained in fair yield by the direct alkaline condensation of veratraldehyde with acetone according to Stobbe and Haertel's method (*loc. cit.*). It was also readily prepared by condensation of 3 : 4-dimethoxystyryl methyl ketone (1·3 g.) with veratraldehyde (1 g.) in alcoholic solution (20 c.c.) in presence of dilute aqueous sodium hydroxide (3 c.c. of 8%); after a few hours, the yellow precipitate was collected and crystallised from alcohol, yielding the pure product, m. p. 84°. A peculiar property of this distyryl ketone was noted: a specimen which had been kept in a sealed tube for several months changed in colour, the golden-yellow crystals becoming yellowish-brown, and crumbled to a powder. The change appeared to start at various centres and slowly spread into the surrounding material, but complete conversion was never attained. The *tetrabromide*, prepared by treating the ketone in chloroform solution with the calculated amount of bromine, crystallised from benzene in colourless needles which darkened at 145° and melted at 152° with inflation [Found: Br, 47·3 (Stepanoff). $C_{21}H_{22}O_5Br_4$ requires Br, 47·4%].

Ethyl 3-mp-*Dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (III).—A solution of 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone (10 g.) and ethyl acetoacetate (4 g.) in boiling alcohol (75 c.c.) was treated with sodium ethoxide (0·4 g. of sodium in 25 c.c. of alcohol) and maintained at the boiling point for 5 minutes. The crystalline solid which separated on cooling (yield, above 90%) was twice recrystallised from absolute alcohol, in which it was sparingly soluble, giving bright yellow needles, m. p. 160—161° (Found: C, 69·3; H, 6·5. $C_{27}H_{30}O_7$ requires C, 69·5; H, 6·4%).

3-mp-*Dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one* (II).—The above-mentioned ester (5 g.), dissolved in glacial acetic acid (75 c.c.), was boiled with 20% sulphuric acid (50 c.c.) under reflux for 4 hours. After cooling, the dark red liquid was slowly poured into ice-water (1000 c.c.). The greenish-yellow, curdy precipitate was crystallised from alcohol and then twice from ethyl acetate. The cyclo*hexenone* formed minute, pale yellow

needles, m. p. 168°, which tenaciously retained traces of ethyl acetate. For analysis, the substance was heated in a vacuum at 100° for several hours. It readily absorbed two molecules of bromine, but no pure bromo-derivative could be isolated (Found: C, 73·0; H, 6·4. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6%).

The direct preparation of 3-*mp*-dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one was carried out by the following modification of Francesconi and Cusmano's method (*loc. cit.*). Veratraldehyde (12 g.), dissolved in aqueous acetone (70 c.c.), was treated with sodium hydroxide solution (25 c.c. of 1%). After the mixture had been kept for 2 days in the ice-chest, the solid was separated and twice recrystallised from ethyl acetate; the pure product, m. p. 168°, was then obtained (yield 20%). The filtrate gave on dilution a viscous yellow oil, from which a small quantity of the normal monostyryl ketone (m. p. 85°) was isolated. The compound, m. p. 168°, gave no depression in melting point in admixture with the *cyclo*hexenone prepared as described above, the constitution of which is definitely determined. The *cyclo*hexenone was also prepared by keeping an acetone solution of 3 : 4-dimethoxystyryl methyl ketone, mixed with a few drops of 8% sodium hydroxide solution, at room temperature for several days. The solution slowly darkened and deposited a crystalline, yellow mass which, after recrystallisation from ethyl acetate, was identical with the Francesconi compound (Found: C, 73·1; H, 6·6%; *M*, 396, 395). Both substances were mixed with the synthesised *cyclo*hexenone (II), but no depression in melting point was noted.

Preparation of the cyclo*hexenone semicarbazone.* A solution of the *cyclo*hexenone (2 g.) in glacial acetic acid was treated with semicarbazide acetate. The yellow solution slowly became red and after 3 days the separated solid was filtered off, washed with water, and dried. On boiling with alcohol part dissolved and part was converted into a golden-yellow, crystalline powder; an identical product was obtained from the alcoholic solution. The *monosemicarbazone* forms golden-yellow rhombs, m. p. 226—227° to a red liquid, and regenerates the *cyclo*hexenone on being refluxed with aqueous-alcoholic oxalic acid for several hours (Found: N, 9·2. $C_{25}H_{29}O_5N_3$ requires N, 9·3%).

Dimeride of 3 : 4-*Dimethoxystyryl Methyl Ketone.*—3 : 4-Dimethoxystyryl methyl ketone (20 g.) was heated on a steam-bath with piperidine (30 c.c.) for 24 hours. The solution was diluted with water and acidified, and the resinous precipitate obtained, on repeated treatment with boiling alcohol, yielded a white, amorphous powder. For analysis, the compound, which was obtained only

in very small yield, was precipitated from benzene solution by the gradual addition of light petroleum; m. p. 209—210° (Found: C, 70·2; H, 6·7; *M*, 418. $C_{24}H_{28}O_6$ requires C, 69·9; H, 6·8%; *M*, 412).

3-*Methoxy*-4-*ethoxystyryl Methyl Ketone*.—Ethylvanillin (5 g.), prepared according to Tiemann's method (*Ber.*, 1875, **8**, 1129), was dissolved in alcohol (5 c.c.) and acetone (15 c.c.) and treated with 1% sodium hydroxide solution (20 c.c.). After an hour, a yellow oil commenced to separate which only very slowly became solid. In subsequent experiments, seeding the mixture at this stage brought about a rapid separation of the solid ketone. Recrystallised from dilute alcohol, it formed yellow needles, m. p. 106° (yield, 83%). The ketone was also obtained in a colourless modification having the same melting point by allowing the yellow modification to stand in suspension in water or xylene for several weeks in direct sunlight. Whereas the yellow form gives an intense crimson coloration in concentrated hydrochloric acid, the colourless isomeride dissolves to a yellow solution (Found: C, 70·7; H, 7·0; *M*, 236. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%; *M*, 220). The *semicarbazone* separates from alcohol in pale yellow plates, m. p. 208—209° (Found: N, 15·4. $C_{14}H_{19}O_3N_3$ requires N, 15·2%).

3 : 3′-*Dimethoxy*-4 : 4′-*diethoxydistyryl Ketone*.—Ethylvanillin (5 g.) and acetone (1 c.c.) were dissolved in 50% alcohol (100 c.c.) together with 10% sodium hydroxide solution (2·5 c.c.) and the mixture was left at room temperature for 24 hours. The yellow precipitate was recrystallised from alcohol, the pure *ketone* separating in yellow needles, m. p. 123—124° (yield, 50%) (Found: C, 72·0; H, 6·8. $C_{23}H_{26}O_5$ requires C, 72·2; H, 6·8%).

Dimeride of 3-*Methoxy*-4-*ethoxystyryl Methyl Ketone*.—The styryl ketone (19 g.) was refluxed on a steam-bath with piperidine (30 c.c.) for 24 hours. The gummy precipitate formed on addition of water was repeatedly washed with alcohol, whereby resinous impurities were wholly removed. The polymeride was purified by slow precipitation from benzene solution by means of light petroleum. It formed a white, amorphous powder, m. p. 187° (yield, 5%) (Found: C, 70·9; H, 7·4; *M*, 446, 465. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%; *M*, 440).

Propylvanillin.—A mixture containing the potassium salt of vanillin (19 g.), propyl iodide (25 g.), and absolute alcohol (20 c.c.) was heated for 12 hours under reflux on the water-bath. After removal of part of the alcohol, the residue was poured into water; the precipitated oil rapidly solidified. This was dissolved in ether and repeatedly washed with dilute alkali solution to remove unchanged vanillin. The residue left after removal of the ether was

recrystallised from dilute alcohol, *propylvanillin* being obtained in colourless crystals, m. p. 59—60° (yield, 60%) (Found: C, 67·8; H, 7·4. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The *semicarbazone* separated from alcohol in colourless needles, m. p. 156° (Found: N, 16·9. $C_{12}H_{17}O_3N_3$ requires N, 16·7%).

3-*Methoxy*-4-*propoxystyryl Methyl Ketone*.—A solution of propylvanillin (2 g.) in acetone (8 c.c.) and alcohol (3 c.c.) was treated with 1% aqueous sodium hydroxide (8 c.c.). The product, which rapidly separated, was twice recrystallised from alcohol, the pure styryl ketone forming bright yellow rhombs, m. p. 92—93° (Found: C, 71·9; H, 7·8. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

3-m-*Methoxy*-p-*propoxyphenyl*-5-m-*methoxy*-p-*propoxystyryl*-Δ^5-cyclo*hexen*-1-*one*.—The ketone (10 g.) in acetone (75 c.c.), alcohol (50 c.c.), and water (100 c.c.) was treated with 2*N*-sodium hydroxide (10 c.c.), and the whole left at room temperature for 3 days. The small amount of yellow precipitate crystallised from ethyl acetate in pale yellow needles, m. p. 152—153°. It readily absorbed two molecules of bromine, halochromic colour effects being shown, but no solid tetrabromide could be isolated (Found: C, 74·5; H, 7·6. $C_{28}H_{34}O_5$ requires C, 74·7; H, 7·6%).

iso*Propylvanillin*, prepared in the same way as the *n*-isomeride, formed a pale yellow, viscous liquid, b. p. 150—152°/13 mm. The *semicarbazone* separated from alcohol in colourless needles, m. p. 151—152° (Found: N, 16·6. $C_{12}H_{17}O_3N_3$ requires N, 16·7%).

3-*Methoxy*-4-iso*propoxystyryl methyl ketone*, prepared by the method described for the *n*-isomeride, separated as a yellow oil which only became solid after long standing. It crystallised from aqueous alcohol in yellow flakes, m. p. 51—53°. An acetone–alcoholic solution of the ketone in presence of alkali darkened fairly rapidly, but only resinous material was isolated. The *semicarbazone* formed yellow needles, m. p. 203—204° (Found: N, 14·6. $C_{15}H_{21}O_3N_3$ requires N, 14·4%).

Benzylvanillin, previously prepared by the oxidation of benzyl-*iso*eugenol (Boehringer und Söhne, D.R.-P. 65,937, 1891), is more conveniently prepared by the following method. A thin alcoholic paste of the potassium salt of vanillin (23 g.) was heated under reflux with benzyl chloride (25 g.) for 12 hours. The excess of benzyl chloride was removed by short distillation in steam and the residual oil, which solidified on cooling, was twice recrystallised from alcohol, benzylvanillin being obtained in colourless crystals, m. p. 64—65° (yield, 70%).

3-*Methoxy*-4-*benzyloxystyryl Methyl Ketone*.—A solution of benzylvanillin (5 g.) in acetone (8 c.c.) and alcohol (20 c.c.) was treated

with sodium hydroxide solution (8 c.c. of 0·5%) and kept in the ice-chest; an oil then separated which slowly solidified. The crude product (yield, 80%) contained a small amount of the corresponding distyryl ketone, which was only separated with difficulty by fractional crystallisation either from alcohol or ethyl acetate. The *ketone* crystallised from alcohol in yellow needles, m. p. 93° (Found: C, 76·4; H, 6·4; *M*, 280, 285. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%; *M*, 282). The *semicarbazone* formed a yellow powder, m. p. 200—201° (Found: N, 12·4. $C_{19}H_{21}O_3N_3$ requires N, 12·4%).

3 : 3′-*Dimethoxy*-4 : 4′-*dibenzyloxydistyryl Ketone*.—A solution of benzylvanillin (2 g.) in acetone (0·5 c.c.) and alcohol (30 c.c.) was treated with 1% sodium hydroxide solution (10 c.c.). After 24 hours, the mixture was neutralised with dilute acetic acid, whereupon an oil separated which rapidly solidified. The distyryl ketone crystallised from ethyl acetate in golden-yellow needles, m. p. 155°. Alternatively, the same compound may be obtained by condensation of 3-methoxy-4-benzyloxystyryl methyl ketone with benzylvanillin (Found: C, 78·1; H, 6·0. $C_{33}H_{30}O_5$ requires C, 78·3; H, 5·9%). The *tetrabromide*, obtained by treating the ketone in chloroform solution with the calculated amount of bromine, formed minute, colourless needles, m. p. 141° (decomp.), from benzene. This compound rapidly decomposes with loss of bromine.

An apparent isomeride of this distyryl ketone was isolated in an attempt to prepare the *cyclo*hexenone from 3-methoxy-4-benzyloxystyryl methyl ketone by the action of alkali in the following manner. The monostyryl ketone (10 g.) in acetone (36 c.c.) and alcohol (36 c.c.) was treated with 8% sodium hydroxide solution (25 c.c.), and the mixture was kept at room temperature for 6 hours and in the ice-chest for 2 days. A solid separated which, after three recrystallisations from ethyl acetate, was obtained in dark orange-yellow needles, m. p. 174—175°. This substance absorbs 2 molecules of bromine, but no solid bromide could be isolated (Found: C, 78·3; H, 6·2%).

Phenyl 3 : 4-*Dimethoxystyryl Ketone*.—A solution of veratraldehyde (5·6 g.) and acetophenone (4 g.) in alcohol (30 c.c.) was treated with 10% sodium hydroxide solution (12 c.c.). After an hour, an oil separated which slowly solidified; in subsequent experiments, seeding of the oil brought about almost instantaneous solidification. The chalkone separated from aqueous alcohol in yellow needles, m. p. 88° (yield, 70%) (Found: C, 75·9; H, 6·3. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%). Attempts to condense this compound to a *cyclo*hexenone by means of alkali failed, only resinous material being formed.

In conclusion, we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) and also to the Cumberland County Council for the renewal of a scholarship (F. I.) which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, June 8th,* 1927.]

CCXLIV.—*The Oxidation of* n-*Triacontane.*

By FRANCIS FRANCIS and NORMAN EDWARD WOOD.

IT is now known that Scotch paraffin wax fusing between 55° and 56°, and probably all similar waxes, are composed of ten to twelve *n*-hydrocarbons (J., 1926, 1420).

The oxidation of paraffin by air or oxygen has been described in this Journal, but in 1922 (J., **121**, 501) it was shown that the synthetic hydrocarbons *n*-hexadecane and *n*-dotriacontane in the presence of 5% of turpentine suffered no change when treated with a current of air at 100° for 730 and 696 hours, respectively. Under similar conditions, paraffin wax reached a content of about 19% of oxygen. At that time, these observations led to the conclusion that the hydrocarbons present in the latter substance differed from those of the normal series.

Later it was found, however, that the presence of very small quantities of certain impurities in paraffin was capable of greatly prolonging the latent phase of the oxidation process, that characteristic period in this reaction when no change is observed.

Both of the above hydrocarbons had been synthesised from their halogen derivatives—octyl and cetyl iodide—purified by the ordinary method, and were judged from their constants and analyses to be pure. A sufficient amount of the specimen of hexadecane used in the work was available, and on being tested was found to contain traces of iodine, and there is but little doubt that the dotriacontane was contaminated in a similar manner. It was highly probable that these impurities had prolonged the latent period of the oxidation, and in order to test this view, a suitable hydrocarbon—*n*-triacontane—was synthesised by a method that did not involve the use of halogen derivatives.

Triacontane was prepared by the electrolysis of potassium palmitate (Peterson, *Z. Elektrochem.*, 1906, **12**, 141). The palmitic acid used was Kahlbaum's purest preparation, and the resulting hydrocarbon (480 g.) was purified by crystallisation from benzene, followed by fractional distillation in a vacuum. It fused at 66·5°, and boiled at 304° (corr.)/15 mm.; the analysis is given in Table I.

During this preparation, about 70 g. of a hydrocarbon were isolated, liquid at the ordinary temperature, a description of which will be given in a later communication.

When triacontane and 5% of turpentine were treated at 95° ± 2° with a current of air free from moisture and carbon dioxide, oxidation took place in a manner strikingly similar to that shown by paraffin wax or the hydrocarbons isolated from it. The analysis of the material after the passage of air for various periods is given in Table I, *a* being the duration of the air current in hours. The final product showed an acid value of 88·6.

TABLE I.

Oxidation of $C_{30}H_{62}$. $t = 95° \pm 2°$.

a.	% C.	% H.	% O by diff.	*a*.	% C.	% H.	% O by diff.
Hydrocarbon	84·9	14·9	—	506	80·5	13·6	5·9
173	82·5	14·5	3·0	577	79·1	13·0	7·9
266	82·4	14·5	3·1	748	78·0	12·8	9·2
341	82·3	14·3	3·4	865	76·1	12·6	11·3
413	81·3	14·0	4·7	1009	75·7	12·2	12·1

If the data in Table I be compared with those for paraffin wax at 100° (J., 1924, **125**, 387), it will be seen that in both cases there is a halt in the progress of the oxidation when the oxidised material contains about 3% of oxygen, and a similar but less well-marked phenomenon when the content has reached 8% of this element.

With the above hydrocarbon at the temperature mentioned, an oxygen content of 7% is reached in 550 hours; at 100°, paraffin wax requires 790 hours, the hydrocarbon $C_{22}H_{46}$ isolated from paraffin 460 hours, and $C_{29}H_{60}$ from the same source 420 hours (compare J., 1924, **125**, 383).

Products of the Oxidation.—(1) During the oxidation of paraffin wax, of the hydrocarbons isolated from it, and of triacontane itself, carbon dioxide and formic acid are formed. The amounts of these were determined by passing the gases through an excess of barium hydroxide solution. Triacontane gave 4·3 g. of carbon dioxide per 100 g. of hydrocarbon oxidised, and in the other cases the amount varied between 4·6 and 6·3 g. The amount of carbon in the form of formic acid produced from triacontane was 0·6 g. per 100 g. oxidised, and in the other cases varied between 1·0 and 1·3 g.

(2) The products of the oxidation were freed from unoxidised triacontane by several crystallisations from fifteen times the volume of acetone. The unchanged hydrocarbon, insoluble in this solvent, amounted to 21%. In the case of paraffin wax under comparable conditions, the corresponding amount lies between 25 and 30%.

(3) The oxidised triacontane, consisting of acids and inert material, was then saponified with an alcoholic solution of caustic potash, water added until 50% was present, and the inert products were extracted with large quantities of light petroleum. The acids amounted to 64%, whereas in the case of paraffin wax they lay between 58 and 69% in different experiments.

Acidic Products of the Oxidation.—(1) The acids were steam-distilled, but the amount of oily distillate was too small for identification. The water in the distilling flask, however, had dissolved a small quantity of a substance which consisted chiefly of succinic acid, although the amount isolated was insufficient for complete purification. It fused at 176°, and at 178—179° when mixed with succinic acid (m. p. 181°), and its molecular weight by titration was 119 (Found: C, 41·2; H, 4·3. Calc. for $C_4H_6O_4$: C, 40·7; H, 5·1%; *M*, 118).

(2) The cake of dry acids from the previous operation was recrystallised several times from chloroform followed by acetone, and about 9% of a mixture of white, crystalline acids was obtained. After long-continued fractional crystallisation, these were found to consist chiefly of $C_{26}H_{52}O_2$, which appeared to be identical with cerotic acid, and a small quantity of $C_{24}H_{48}O_2$. Both these acids had been previously isolated in this laboratory from products of the oxidation of paraffin wax.

The specimen of cerotic acid used for the comparison was prepared for us by the Eastman Kodak Co. It had been isolated from beeswax and purified by the fractionation of its methyl ester. Both this acid and the corresponding one mentioned above were further purified by conversion, in methyl-alcoholic solution, into the barium salt, which was extracted with ether and finally with acetone. The acids recovered from these salts by solution in hot acetic acid were repeatedly crystallised from acetone and finally from light petroleum. The full comparison is given in Table II.

The data given for the corresponding acids from paraffin wax (*a*) and (*b*) were for specimens isolated by different observers and their preparation will be described in another communication. We have to thank Mr. Piper, who is undertaking an investigation of these other acids, for the *X*-ray data. He informs us that, as regards the high values in the above table, the error is about 1%. We point out that the melting points of the above acids are about 10° lower than that of the synthetic acid of the same carbon content, which, according to Levene and Taylor, fuses at 88·5° (*J. Biol. Chem.*, 1924, **59**, 919). We leave to a later date the discussion of this acid and that melting at 74°, of acid value 152, which is probably $C_{24}H_{48}O_2$, together with a series of what are believed to be

TABLE II.

Source.	Beeswax.	$C_{30}H_{62}$.	Paraffin wax. (*a*).	Paraffin wax. (*b*).
M. p.	77·5°	78°	80°	76°
Mixed m. p.	77·5—78°			
Acid value. (Calc. for $C_{26}H_{52}O_2$, 141)	144	145	141	146
Calc. for $C_{26}H_{52}O_2$ { C 78·8%	78·6%	78·4%	79·1%	78·9%
Calc. for $C_{26}H_{52}O_2$ { H 13·1%	13·1%	13·2%	13·3%	13·1%
X-Ray spacing, "pressed." Å.	68·03	68·85	68·8	68·4
M. p. of methyl ester. (Previous observers, 60—62°)	60·5°	63·5°	62—3°	62°
Mixed m. p.	62°			
M. p. of ethyl ester. (Previous observers, 59—60°)	58°	60·5°		
Mixed m. p.	59°			
X-Ray spacing, "pressed." Å. Ethyl ester.	39·15	39·0		

analogous acids, which have been isolated from the oxidation products of paraffin wax.

(3) The main bulk of the acids, from which cerotic acid and the acid $C_{24}H_{48}O_2$ have been removed, is a complex mixture of monobasic and oxy-acids which cannot be separated from the small amount of inert material present by conversion into barium salts and extraction with solvents. The mixture is as difficult to deal with as that of the corresponding material from paraffin wax.

The material was converted into methyl esters, of which about 38% could be distilled without decomposition in a vacuum of 3 mm., this amount corresponding closely with that observed in the case of the similar complex obtained from paraffin wax. The distillate boiled between 140° and 205°/6 mm. and on standing in the ice-chest deposited a crystalline substance. The acids obtained from this were fractionally crystallised from acetone and finally two were isolated in small quantities: (A) M. p. 63°, acid value 188. Found: C, 76·1, 76·3; H, 12·7, 12·7%. The pressed *X*-ray spacings were Å. 52·11. Provisionally this is regarded as $C_{20}H_{40}O_2$ (Calc.: Acid value, 179; C, 76·9; H, 12·8%). (B) M. p. 53·4°. Found: C, 74·8, 75·0; H, 12·5, 12·4%. The pressed *X*-ray spacings = Å. 46·56. This is provisionally regarded as $C_{16}H_{32}O_2$ (Calc.: C, 75·0; H, 12·5%), but is probably contaminated with an acid of higher carbon content.

(4) The residue of esters which could not be distilled gave a

small quantity of an acid, fusing at 68° after repeated crystallisation from glacial acetic acid (Found : C, 76·9; H, 12·6%). It is probably an impure specimen of $C_{22}H_{44}O_2$ (Calc. : C, 77·6; H, 12·9%).

Acids similar to those just described have been isolated in larger quantities from the products of the oxidation of paraffin wax.

Inert Products of the Oxidation.—Following the method previously described (J., 1926, 2377), the non-acidic products of the oxidation were repeatedly crystallised from five times their weight of acetone, and thus separated into a relatively insoluble, white, crystalline mass, comprised chiefly of ketones and dioxy-products constituting together about 46% of the mixture, and a more soluble coloured mixture of more highly oxidised hydrocarbon, which was not further examined.

(i) The crystalline mixture fused at 58—59°. It was acetylated and the more soluble acetyl derivatives were separated by their greater solubility in acetone. The acetates were decomposed, and the resulting alcohol after purification fused at 69° (Found : C, 79·4; H, 13·5. Calc. for $C_{30}H_{60}O_2$: C, 79·6; H, 13·2%). It was either a ketonic alcohol or a dihydroxy-derivative, but the amount obtained was insufficient for further examination. The residual material, from which a certain part of the dioxy-substance had been separated, fused at 60—61° and contained C, 80·7; H, 14·2%. It was chiefly composed of ketones and dioxy-derivatives.

(ii) This mixture was treated with hydroxylamine, and the resulting oxime separated by its greater solubility in alcohol from the other substances present. The oxime itself could not be purified, but on saponification it gave a well-defined, crystalline ketone, m. p. 62·5° (Found : C, 82·0; H, 13·8. Calc. for $C_{30}H_{60}O$: C, 82·5; H, 13·7%).

Mr. Piper examined this specimen by *X*-rays and informed us that it contained 30 carbon atoms and, judging from the intensity distribution, the oxygen was situated most probably on the fourth carbon atom. (See J., 1926, 2381, for corresponding ketones with lower carbon content obtained from paraffin wax.)

Summary.

We have shown the striking similarity between the oxidation of synthetic triacontane, the mixture of solid *n*-hydrocarbons termed paraffin wax, and the pure constituents isolated from the latter. This similarity extends, not only to the velocity of oxidation, but to the nature and amounts of the products formed.

The highest acid present among the acidic products of the oxidation of triacontane has a carbon content of 26 atoms and appears to be identical with cerotic acid obtained from beeswax. This

acid fuses 10° lower than the corresponding synthetic acid, a phenomenon noticed with other acids obtained from paraffin wax, which will be discussed at a later date.

Support has been obtained for the view expressed previously (J., 1926, 2383) that in the oxidation of hydrocarbons such as triacontane the first product is a secondary alcohol, which then passes to a ketone. The latter has been isolated and found to have a carbon content of 30 atoms. *X*-Ray analysis indicates that the oxygen is situated on the fourth carbon atom; on further oxidation, the chain breaks, and the fact that a C_{26} acid results leads to the conclusion that the ketone has the structure

$$CH_3 \cdot [CH_2]_{24} \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_3.$$

This view is also supported by the presence of succinic acid among the products of the reaction.

The amount of acids with high carbon content resulting from the oxidation of such long-chain hydrocarbons is always very small. Probably, simultaneously with the formation of the secondary alcohol followed by that of the ketone and their breakdown into acids, there occurs the further oxidation of the mono-oxy-derivative first formed to polyhydroxy-derivatives, which on further oxidation pass to ketones and then break down to acids and oxy-acids of still smaller carbon content.

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UNIVERSITY OF BRISTOL. [*Received, June 1st,* 1927.]

CCXLV.—*The Isomeric Hydroxybenzyldimethylamines.*

By EDGAR STEDMAN.

A SEPARATE problem necessitated the synthesis of the isomeric hydroxybenzyldimethylamines, which was effected by treating the methoxybenzyl bromides with dimethylamine and hydrolysing the methoxybenzyldimethylamines so prepared with hydrobromic acid —a method similar to that employed by Tiffeneau (*Bull. Soc. chim.*, 1911, **9**, 825) for the preparation of the *p*-isomeride. Previous unsuccessful attempts had been made to prepare these phenols from the nitrobenzyl chlorides. Dimethylamine converted the latter into the nitrobenzyldimethylamines, which, on reduction, gave the aminobenzyldimethylamines. These underwent smooth diazotisation, but no phenol could be isolated from the tarry product obtained by decomposing the diazo-compound in hot aqueous solution.

In the interaction between *p*-nitrobenzyl chloride and dimethylamine, a considerable quantity of di-*p*-nitrobenzyldimethylammonium chloride was produced, whilst only insignificant amounts (if any) of such quaternary salts were formed from the *o*- and *m*-isomerides. Although the reactions were not carried out under the same conditions of concentration, this result agrees with the recent experiments of McCombie, Scarborough, and Smith (this vol., p. 802), who have shown that the velocity coefficient for the formation of quaternary salts from trimethylamine and the nitrobenzyl chlorides is greater in the case of the *p*- than of the *o*- and *m*-isomerides.

EXPERIMENTAL.

o-, m-, *and* p-*Hydroxybenzyldimethylamine.*—A solution of the methoxybenzylbromide in benzene was prepared by saturating a benzene solution of the methoxybenzyl alcohol with dry hydrogen bromide, drying it over anhydrous calcium bromide, and distilling off benzene until most of the excess hydrobromic acid had been removed (compare Lapworth and Shoesmith, J., 1922, **121**, 1391). Excess of a solution of dimethylamine in benzene was then added and after 24 hours the dimethylamine bromide which had separated was removed by filtration and the methoxybenzyldimethylamine extracted from the benzene solution with hydrochloric acid. Traces of benzene were removed from the acid solution by extraction with ether, and the base was liberated with sodium hydroxide and extracted with ether. Evaporation of the dried ethereal extract gave the methoxybenzyldimethylamine, which, after being distilled under diminished pressure, was converted into the hydroxybenzyldimethylamine by boiling with constant-boiling hydrobromic acid. In the case of the *m*-compound, 4 hours sufficed completely to hydrolyse the methoxy-group. The hydrobromic acid was removed by distillation under diminished pressure, the residue dissolved in water and made alkaline with sodium carbonate, and the phenol shaken out with ether. The product obtained on evaporation of the dried ethereal extract rapidly crystallised. In the case of the *o*- and *p*- compounds, the treatment with hydrobromic acid was continued for 10 hours. Nevertheless, hydrolysis was incomplete and considerable decomposition occurred with the *p*-isomeride. In both cases, the product left after removal of the hydrobromic acid was dissolved in water, and the solution was extracted with ether before and after being made alkaline with sodium hydroxide in order to remove impurities and unchanged methoxy-compound. It was then made slightly acid and the phenol was precipitated with sodium carbonate and shaken out with ether. Evaporation of the dried ethereal extract gave the phenols in fairly pure form.

m-*Methoxybenzyldimethylamine* is a colourless oil, b. p. 105°/13 mm. The *hydrochloride* crystallises from acetone–alcohol in tablets, m. p. 173° (Found: Cl, 17·6. $C_{10}H_{15}ON,HCl$ requires Cl, 17·6%).

m-*Hydroxybenzyldimethylamine* crystallises from benzene in prisms, m. p. 108°. The *hydrochloride* crystallises from alcohol in flat prisms, m. p. 173° (Found: Cl, 18·9. $C_9H_{13}ON,HCl$ requires Cl, 18·9%).

p-Methoxybenzyldimethylamine has b. p. 109°/13 mm. (compare Tiffeneau, *loc. cit.*). The *hydrochloride* crystallises from acetone in prisms, m. p. 152° (Found: Cl, 17·6%).

p-Hydroxybenzyldimethylamine (compare Tiffeneau) has m. p. 106°. The *hydrochloride* separates from alcohol in macroscopic prisms, m. p. 185° (Found: Cl, 18·7%).

o-*Methoxybenzyldimethylamine* is a colourless oil, b. p. 113°/20 mm. The *hydrochloride* is hygroscopic. After crystallisation from acetone, it has m. p. 149° (Found: Cl, 17·7%).

o-*Hydroxybenzyldimethylamine* is a colourless oil, b. p. 99—100°/12 mm. The *methiodide* crystallises from alcohol in prisms, m. p. 169° (Found: I, 43·1. $C_9H_{13}ON,CH_3I$ requires I, 43·35%).

o-*Nitrobenzyldimethylamine.*—An alcoholic solution of 30 g. of *o*-nitrobenzyl chloride was treated with dimethylamine (slightly more than 2 mols.) dissolved in the same solvent. After 3 days, the alcohol was evaporated, and the residue treated with water and sufficient hydrochloric acid to produce a clear solution. After extraction with ether to remove any unchanged nitrobenzyl chloride, the solution was made alkaline with sodium carbonate and the oil thus precipitated shaken out with ether. Evaporation of the dried ethereal extract left 29·1 g. of an oil. This was converted directly into the hydrochloride (yield 33 g.). When recrystallised from alcohol–acetone, the *hydrochloride* of o-*nitrobenzyldimethylamine* forms long, almost colourless prisms, m. p. about 221° (Found: Cl, 16·4. $C_9H_{12}O_2N_2,HCl$ requires Cl, 16·4%).

o-*Aminobenzyldimethylamine.*—The hydrochloride (10 g.) of *o*-nitrobenzyldimethylamine was mixed with 17 g. of granulated tin, and 70 g. of concentrated hydrochloric acid were added slowly in small portions, with efficient cooling. The solution was finally heated on the water-bath for 30 minutes and then cooled. The crystalline stannichloride which had separated was filtered off and decomposed in aqueous solution by hydrogen sulphide, the filtrate from the tin sulphide was boiled to expel the excess of hydrogen sulphide and made alkaline with sodium carbonate, and the oil thus precipitated was extracted with ether. Evaporation of the dried ethereal extract left 4 g. of a somewhat brown oil which slowly crystallised. (A further 1·6 g. was obtained by working up

the filtrate from the stannichloride in a similar manner.) This was distilled under diminished pressure; o-*aminobenzyldimethylamine*, b. p. 107°/14 mm., then passed over as a colourless oil which crystallised completely on cooling. The crystals had m. p. 36—37°. The *dihydrochloride* separates from alcohol in blunt prisms, m. p. 205° after sintering at 193° (Found: Cl, 31·7. $C_9H_{14}N_2,2HCl$ requires Cl, 31·8%).

Action of Dimethylamine on p-*Nitrobenzyl Chloride.*—A mixture of dimethylamine (slightly more than 2 mols.) and *p*-nitrobenzyl chloride (30 g.) in alcoholic solution was kept for 3 days. The alcohol was then evaporated, and the residual brown oil treated with water and sufficient hydrochloric acid to produce a clear solution. Ether extracted from this a small quantity of a red oil. Addition of sodium carbonate to the aqueous solution precipitated an oil which partly solidified. Extraction with ether removed the oil, but not the solid. On evaporation of the dried ethereal extract, an orange oil (20·8 g.) was obtained. This was converted directly into the hydrochloride, but only 14 g. could be obtained in solid form. The *hydrochloride* of *p*-nitrobenzyldimethylamine thus prepared crystallised from acetone–alcohol in faintly yellow plates, m. p. 188° (Found: Cl, 16·3. $C_9H_{12}O_2N_2,HCl$ requires Cl, 16·4%). The base was recovered from the oily residue from the preparation of the hydrochloride and divided into two portions, one of which was treated with methyl iodide. This yielded p-*nitrobenzyltrimethylammonium iodide*, which crystallised from alcohol in yellow, wedge-shaped prisms, m. p. 198° (Found: I, 39·1. $C_9H_{12}O_2N_2,CH_3I$ requires I, 39·4%). The second portion of the recovered base was treated with an alcoholic solution of oxalic acid; the *oxalate* of *p*-nitrobenzyldimethylamine was thus obtained, which separated from alcohol in lustrous, yellow plates, m. p. 155°. The identities of the oxalate and methiodide were established by recovering the base from the oxalate and converting separate portions into its methiodide and hydrochloride. The salts obtained were identical with those described above.

The above-mentioned solid which was not extractable with ether was filtered off (yield 8·8 g.) and recrystallised from alcohol; it then formed stout prisms, m. p. about 176°. Its behaviour was that of a quaternary chloride, for it was soluble in water and its aqueous solution contained ionic chlorine, but gave no precipitate on addition of alkalis. Analysis indicated that it was *di*-p-*nitrobenzyldimethylammonium chloride* (Found: Cl, 10·1. $C_{16}H_{18}O_4N_3Cl$ requires Cl, 9·8%).

p-Aminobenzyldimethylamine, prepared as in the case of the *m*-isomeride, has b. p. 133°/16 mm. (compare Friedländer and

Moszyc, *Ber.*, 1895, **28**, 1141). The *dihydrochloride* separates from alcohol in needles, m. p. 216° (Found: Cl, 31·7. $C_9H_{14}N_2,2HCl$ requires Cl, 31·8%).

m-*Nitrobenzyldimethylamine* was prepared from *m*-nitrobenzyl chloride (20 g.) and dimethylamine as in the case of the *o*-isomeride, 19·1 g. of a yellow oil being obtained. This was converted directly into the hydrochloride (yield 23 g.). When recrystallised from alcohol, the *hydrochloride* of *m*-nitrobenzyldimethylamine forms practically colourless, stout prisms, m. p. 230° (Found: Cl, 16·3. $C_9H_{12}O_2N_2,HCl$ requires Cl, 16·4%).

m-*Aminobenzyldimethylamine* was prepared by the method employed for the *o*-isomeride. 10 G. of the hydrochloride of the nitro-compound yielded a crystalline stannichloride which, on decomposition with hydrogen sulphide, gave 3 g. of the base. On distillation, it was obtained as a colourless oil, b. p. 129°/13 mm., which rapidly crystallised. The crystals had m. p. 46°. The *dihydrochloride* crystallised from alcohol in prisms, m. p. 225° after sintering at 210° (Found: Cl, 31·7. $C_9H_{14}N_2,2HCl$ requires Cl, 31·8%).

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DEPARTMENT OF MEDICAL CHEMISTRY,
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CCXLVI.—*The Effect of Hydrochloric Acid on the Electrode Potential between Mercury and Mercurous Chloride.*

By SYDNEY RAYMOND CARTER, FREDERICK MEASHAM LEA, and ROBERT ANTHONY ROBINSON.

THE effect of hydrochloric acid on the electrode potential between mercury and calomel has been investigated by Sauer (*Z. physikal. Chem.*, 1904, **47**, 146), who worked with 0·1*N*- and 1·0*N*-solutions of hydrochloric acid. Measurements have also been made by Tolman and Ferguson (*J. Amer. Chem. Soc.*, 1912, **34**, 232), Ellis (*ibid.*, 1916, **38**, 737), and Linhart (*ibid.*, 1917, **39**, 2601), on cells of the type:

$$H_2|xN\text{-HCl, solid } Hg_2Cl_2|Hg$$

combined with a similar cell using *N*-hydrochloric acid, the whole forming a concentration cell without transport, reversible with respect to both the chlorine and the hydrogen ions.

Direct measurements of cells of the type :

$$Hg|Hg_2Cl_2,xN\text{-}HCl|N\text{-}HCl|N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg$$

have now been carried out, a correction being applied for the diffusion potential across the boundary xN-HCl|N-HCl on the basis of some earlier results (Carter and Lea, J., 1925, **127**, 487). Measurements of this type have been employed to elucidate certain results which are described in the succeeding communication.

Construction of Cells.—Mercurous chloride was obtained in a state of purity, containing no mercuric chloride and only a trace of free mercury. The mercury used was purified both by electrolytic methods and by distillation. Cell solutions were prepared by grinding calomel, together with a little free mercury, into a paste with hydrochloric acid of a known concentration. The supernatant liquid was decanted repeatedly as in the construction of the normal calomel electrode. The electrode was of mercury, and upon this was placed a thin layer of calomel paste, the vessel being filled with hydrochloric acid solution saturated with calomel. The following chain of solutions was constructed :

$$\underset{\leftarrow E}{Hg|Hg_2Cl_2,xN\text{-}HCl}\,|\,\underset{\rightarrow \pi}{xN\text{-}HCl}\,|\,\underset{\rightarrow 0\cdot0288}{N\text{-}HCl}\,|\,N\text{-}KCl\,|\,N\text{-}KCl,\underset{\rightarrow 0\cdot560}{Hg_2Cl_2|Hg}$$

$$\leftarrow E_c$$

Special experiments were made in order to ascertain that the diffusion potentials were constant over a considerable period of time and were also reproducible. Several arrangements were tried, but the above was found to be the most satisfactory. Connexion between the solutions at A and B was made by means of inverted U-tubes filled with N-solutions of hydrochloric acid and potassium chloride, respectively, and plugged at both ends with wads of filter paper. The diffusion potential at B can be calculated on the basis of Henderson's formula (*Z. physikal. Chem.*, 1907, **59**, 118) to be 0·0288 volt. That at A has been measured (Carter and Lea, *loc. cit.*) for values of x greater than unity ; for values less than unity it may be calculated from the usual formula. Thus if E is the potential of the half-element, $Hg|Hg_2Cl_2,xN$-HCl, and E_c is the potential of the whole cell, then

$$E = E_c + \pi + 0{\cdot}0288 + 0{\cdot}560 \text{ volt.}$$

All measurements were made at 18°, and the observed *E.M.F.* is regarded as positive if the current flows through the cell from the normal calomel electrode towards the acid solution. An inert atmosphere of nitrogen was maintained in the cells during the experiments.

Results.

The results are given in Table I. The values given under the heading E (obs.) were obtained from the above equation by using the mean of the values given under E_c.

TABLE I.

[HCl].	E_c.			π.	E (obs.).	E (calc.). (Conductivity.)	E (calc.). (Activity.)
10·09	−0·2595			0·0809	0·4102	—	0·4106
10·00	−0·2572,	−0·2576,	−0·2580	0·0806	0·4118	—	0·4112
7·60	−0·2121			0·0706	0·4473	—	0·4436
7·20	−0·2036,	−0·2041,	−0·2045	0·0674	0·4521	—	0·4494
4·64	−0·1460,	−0·1462,	−0·1465	0·0465	0·4891	—	0·4877
4·48	−0·1434			0·0450	0·4904	—	0·4900
2·73	−0·0970,	−0·0975,	−0·0975	0·0263	0·5177	—	0·5184
2·29	−0·0823			0·0205	0·5270	—	0·5263
1·00	−0·0348,	−0·0348,	−0·0349	0·0000	0·5540	0·5579	0·5570
0·10	+0·0590,	+0·0593,	+0·0595	−0·0370	0·6111	0·6137	0·6154
0·0106	+0·1528,	+0·1530,	+0·1531	−0·0731	0·6687	(0·6687)	(0·6687)
0·0027	+0·2121			−0·0974	0·7035	0·7032	0·7019

The potential between mercury and any solution in equilibrium with it is given by the equation:

$$E = E_0 + 0{\cdot}029 \log [Hg_2^{\cdot\cdot}] \quad . \quad . \quad . \quad . \quad (1)$$

Since the solution is saturated with respect to calomel, if the solubility product $[Hg_2^{\cdot\cdot}]\,[Cl']^2 = k_1$, then

$$E = E_0 + 0{\cdot}029 \log k_1/[Cl']^2 =$$

$$E_0 + 0{\cdot}029 \log k_1 - 0{\cdot}058 \log [Cl'] \quad . \quad . \quad (2)$$

or

$$E = E_0' - 0{\cdot}058 \log [Cl'] \quad . \quad . \quad . \quad . \quad (3)$$

The calculated values in the last two columns have been obtained from equation (3) by taking the observed value of $E = 0{\cdot}6687$ volt for $[HCl] = 0{\cdot}0106N$. In column 5, the chlorine-ion concentration has been deduced from conductivity–viscosity data for concentrations up to N-hydrochloric acid, whilst in column 6 it has been obtained from activity data (Lewis and Randall, "Thermodynamics," 1923, p. 336).

The agreement with the observed *E.M.F.* is satisfactory, but it should be pointed out that the agreement in the case of the activities cannot be regarded as an entirely independent proof, since the activity values have been derived primarily from potential measurements of cells which are virtually the same as those under consideration.

Effect of Mercuric Chloride on the Electrode Potential.—It was thought possible that mercuric chloride in presence of mercury might register a measurable potential. When such a cell was constructed from $0{\cdot}05N$-mercuric chloride in $3{\cdot}0N$-hydrochloric acid,

the usual grey film appeared on the surface of the mercury, and the *E.M.F.* measured showed wide fluctuations over several days, but tended towards the same value as the potential of the same cell containing calomel in 3·0*N*-hydrochloric acid. It was therefore concluded that the Hg–Hg$^{\cdot\cdot}$ potential is inaccessible.

The reduction of mercuric chloride by mercury is by no means rapid. Thus two solutions, each containing 13·576 g. of mercuric chloride per litre in 10*N*-hydrochloric acid, were found after 10 days' contact with mercury electrodes to contain 5·648 and 6·558 g. of mercuric chloride per litre, respectively. In more dilute solutions, the reduction is even slower; for instance, a solution of 0·05*M*-mercuric chloride in 7·6*N*-hydrochloric acid contained 12·90 and 12·32 g. of mercuric chloride per litre after 5 and 7 days' contact with mercury, respectively.

It is thus possible to have a considerable quantity of mercuric chloride in contact with mercury and calomel for a long time before equilibrium is reached, and it should therefore be possible to determine the effect of mercuric chloride on the electrode potential 2Hg–$Hg_2^{\cdot\cdot}$.

Cells were constructed containing 0·05*M*-mercuric chloride, in varying concentrations of hydrochloric acid saturated with calomel, in contact with mercury. In Table II E_c' is the *E.M.F.* of the cell

TABLE II.

[HCl].	E_c'.	E_c.	[HCl].	E'.	E_c.
10·09	−0·2551	−0·2595	0·160	+0·0687	+0·0507
7·60	−0·2070	−0·2121	0·0137	+0·1625	+0·1514
5·37	−0·1565	−0·1635	0·0027	+0·2292	+0·2121
2·29	−0·0676	−0·0823			

containing 0·05*M*-mercuric chloride, and E_c that of the cell free from mercuric chloride. Both potentials represent that of the whole cell, including that of the normal calomel electrode. It will be seen that the effect of 0·05*M*-mercuric chloride on the *E.M.F.* is always small and is least in the higher concentrations of acid. The effect of mercuric chloride is to decrease the chlorine-ion concentration owing to the formation of complex ions, and from equation (2) it may be seen that this results in an increase in the *E.M.F.*

Potentials registered at an Inert Electrode.—Richards and Archibald (*Z. physikal. Chem.*, 1902, 40, 385) have shown that a definite equilibrium exists between the components of the system

$$Hg–Hg_2Cl_2–HgCl_2,$$

provided that the three are present together; the active masses of the first two are definite but beyond analytical detection, whilst the concentration of mercuric chloride in contact with mercury and

calomel has been determined and found to be dependent on the acid concentration. If, therefore, pure mercurous chloride is brought into contact with hydrochloric acid solution, it will not be in a state of equilibrium, but will tend to decompose with separation of metallic mercury and mercuric chloride, the process going on until the equilibrium concentration of mercuric chloride is reached. At this point, as the three components are in equilibrium, the three potentials $E_{2Hg\text{-}Hg_2^{\cdot\cdot}}$, $E_{Hg_2^{\cdot\cdot}\text{-}2Hg}$, and $E_{Hg\text{-}Hg^{\cdot\cdot}}$ will be equal, hence the electrode potential between a mercury electrode and the mercurous ions measured in the above series should be equal to the oxidation potential between mercurous and mercuric ions measured at an inert platinum electrode. Measurements of this nature have been carried out. By the use of hydrochloric acid solutions of 4·6*N*, 7·2*N*, and 10·0*N*, it was found that the potentials at a platinum electrode in a solution saturated with calomel and containing concentrations of mercuric chloride less than the equilibrium concentration were identical with the electrode potentials registered above. Moreover, the mercuric chloride concentration increased until it reached the equilibrium concentration. If, however, the initial mercuric chloride concentration was greater than this, then no further increase occurred, and, moreover, the potential registered —presumably the oxidation potential—was greater than the corresponding electrode potential. Since the oxidation potential is proportional to log [$HgCl_2$], any further increase in the mercuric chloride concentration beyond the equilibrium point will result in a continuous increase in the potential. Thus it was found (compare Fig. 1, following paper) that if the potential were plotted against log [$HgCl_2$], the curve obtained was a straight line parallel to the log [$HgCl_2$] axis for low values of [$HgCl_2$], but it exhibited a definite break at the [$HgCl_2$] value corresponding to the equilibrium point, and then rose sharply.

Table III gives a comparison between the values of the equilibrium concentrations of mercuric chloride which we observed (C., L., and R.) and the values found by Richards and Archibald (R. and A.).

TABLE III.

[HCl]	4·60	5·48	7·20	7·30	10·0*N*
[$HgCl_2$] (R. and A.)	—	0·0020	—	0·0025	0·0025*M*
[$HgCl_2$] (C., L., and R.).	0·0021	—	0·0021	—	0·0019*M*

Thus for [$HgCl_2$] values less than the equilibrium concentration the oxidation potential is less than the electrode potential and the latter is registered both at a mercury electrode and at an inert electrode. At the equilibrium point, they are equal to one another, and for higher concentrations of mercuric chloride the electrode

potential is registered at a mercury electrode and the higher oxidation potential at an inert platinum electrode.

In lower acid concentrations (0·01*N*—2·7*N*), this agreement could not be obtained. Richards and Archibald found that the equilibrium concentration of mercuric chloride in 1·0*N*- and 2·7*N*-hydrochloric acid was 0·00017*M* and 0·00076*M*, respectively. Cells constructed containing these concentrations of mercuric chloride were found to yield potentials against platinum electrodes which were, respectively, higher than the corresponding electrode potentials by 0·071 and 0·023 volt. It is probable, therefore, that in solutions which are dilute with respect to both the acid and the mercuric chloride the potential registered at the platinum electrode does not represent the true reversible oxidation potential. It was found that the same potential was registered whether the electrodes were platinised or not. Moreover, the presence of a single platinum electrode did not alter the equilibrium concentration of mercuric chloride which at 18° in *N*-hydrochloric acid was at 0·00022*M*-mercuric chloride. If, however, several electrodes (*e.g.*, four) were placed in the mixture of solution and calomel, an increase in the mercuric chloride concentration to 0·00050*M* occurred, together with the corresponding increase in potential. These phenomena are somewhat obscure and render the measurement of oxidation potentials in very dilute mercuric chloride and hydrochloric acid solutions somewhat uncertain and difficult to interpret.

Summary.

The effect of hydrochloric acid on the electrode potential between mercury and mercurous chloride in hydrochloric acid solution has been investigated over a range of acid concentration from 0·0027*N* to 10·0*N*.

Under the conditions of these experiments, the potential Hg–$Hg^{\cdot\cdot}$ was inaccessible, and the effect of mercuric chloride on the above electrode potential was small.

The equilibrium of the system Hg–Hg_2Cl_2–$HgCl_2$ has been studied in relation to the work of Richards and Archibald, and the potentials registered by this system of platinum electrodes have been described.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCXLVII.—*The Oxidation-Reduction Potentials of Mercurous and Mercuric Chlorides in Hydrochloric Acid Solution.*

By SYDNEY RAYMOND CARTER and ROBERT ANTHONY ROBINSON.

LITTLE attention has hitherto been devoted to the oxidation-reduction potentials of the chlorides of mercury. Although Drucker (*Z. physikal. Chem.*, 1901, **36**, 195; *Z. Elektrochem.*, 1912, **18**, 236) and Baur (*Z. physikal. Chem.*, 1908, **63**, 687) have made a few measurements in potassium chloride solution, a further investigation of the potentials in hydrochloric acid solution is desirable in view of the complicated behaviour of mercury halides in the presence of halogen acids, and also of the recent investigations of Stewart and Wardlaw (J., 1922, **121**, 1481) on the action of sulphur dioxide on these two chlorides which can be correlated with the electrochemical properties of these systems.

EXPERIMENTAL.

Preliminary experiments indicated that it would be a matter of considerable difficulty to obtain steady reproducible potentials corresponding with the oxidation process $Hg_2^{\cdot\cdot} \longrightarrow 2Hg^{\cdot\cdot}$. In the first place, it was found that a 0·1*M*-solution of mercuric chloride saturated with calomel and containing no acid had so low a conductivity that potential measurements were impossible. Secondly, in solutions of 0·1*N*-hydrochloric acid saturated with calomel and containing mercuric chloride, it was found that no agreement could be obtained between the potentials registered at platinised platinum electrodes; moreover, the potential varied widely with time. In a similar solution containing 0·0005*M*-mercuric chloride, a large fall in potential was observed over several days, but after this a reading was obtained which was fairly constant and almost equal to the electrode potential of mercury and calomel in 0·1*N*-hydrochloric acid. Since the electrodes had become covered with a grey deposit of mercury, it was concluded that an electrode and not an oxidation potential was being measured.

A number of similar experiments were performed with the same result. Shaking the calomel with the solution of hydrochloric acid and mercuric chloride for 12 hours did not give a more constant potential reading. It was noticed, however, that if the electrodes were completely buried to a considerable depth in a paste of calomel instead of being suspended in the solution, and if the dissolved air in the solution were removed by means of a current of purified nitrogen, it was possible to obtain potentials which gave good

agreement between different electrodes over considerable periods of time and were reproducible. Moreover, they were distinct from the electrode potentials described in the preceding paper. The necessity for the complete immersion of the electrodes is probably due to the low concentration of mercurous ions, the passage of a very small current in the course of potential measurements being sufficient to exhaust the supply of mercurous ions in the vicinity of the electrode if this is simply suspended in the solution. Complete immersion of the electrode in the paste ensures full saturation in its vicinity.

Cells of the following type were constructed:

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Hg_2Cl_2}\\ x\mathit{M}\text{-}\mathrm{HgCl_2}\\ y\mathit{N}\text{-HCl}\end{matrix}\right|y\mathit{N}\text{-HCl}\left|\mathit{N}\text{-HCl}\right|\mathit{N}\text{-KCl}\left|\mathit{N}\text{-KCl},\mathrm{Hg_2Cl_2}\right|\mathrm{Hg}.$$

The chain of intermediate solutions has been shown to be sufficient to maintain constant reproducible diffusion junctions (Carter and Lea, J., 1925, **127**, 487; Carter, Lea, and Robinson, preceding paper), and possesses the advantage that the potential at each junction can be determined with the necessary degree of accuracy. The system differs from the previously investigated systems of iron and copper salts (Carter and Clews, J., 1924, **125**, 1880; Carter and Lea, J., 1925, **127**, 499) in that only the mercuric chloride and the hydrochloric acid concentrations in the oxidation cell can be subjected to variation, since the calomel cannot be varied in concentration owing to its low solubility. It is essential, however, to maintain the solution saturated with respect to the calomel in order to obtain a defined system.

The oxidation cell consisted of a glass vessel containing a solution of mercuric chloride and hydrochloric acid in the requisite proportion and saturated with respect to calomel. Experiments showed that platinisation of the electrodes did not increase their sensitivity, nor was the shape or form of the electrodes a factor influencing the potential readings. Three electrodes of polished platinum foil (about 1 sq. cm. in area) were actually employed.

Measurements of each of the cells were carried out, in general, over a period of a week, a lapse of 12—24 hours after construction being necessary before a constant potential was registered. Renewal of the liquid boundaries during this period showed that no appreciable change had occurred in the diffusion potentials. All potentials are referred to the absolute scale. A positive sign indicates that the current flows through the cell from the calomel electrode to the oxidation element. All measurements were made at 18°. Concentrations of mercuric chloride are given as g.-mols. per litre.

Potential Measurements.—If E is the potential of the oxidation element, π the diffusion potential between xN- and N-hydrochloric acid (Carter and Lea, *loc. cit.*), 0·0288 volt the diffusion potential between N-hydrochloric acid and N-potassium chloride (calculated on the basis of Henderson's formula, *Z. physikal. Chem.*, 1907, **59**, 118), and E_c the potential of the whole cell, then:

$$E = E_c + \pi + 0{\cdot}0288 + 0{\cdot}560 \text{ volt.}$$

The values for one experiment given in Table I are typical of the degree of accuracy attained.

TABLE I.

Cell made up as: $[HCl] = 1{\cdot}00N$, $[HgCl_2] = 0{\cdot}75M$.
Final composition by analysis: $[HCl] = 0{\cdot}96N$, $[HgCl_2] = 0{\cdot}735M$.

Time (days).	0.	1.	2.	3.	4.	5.
Electrode No. 1	(0·2654)	0·3026	0·2974	0·3012	0·2988	0·3006
„ „ 2	(0·2644)	0·3026	0·2966	0·3006	0·2988	0·3006
„ „ 3	(0·2634)	0·3026	0·2970	0·3012	0·2988	0·3006

Average potential (neglecting readings on first day) = 0·3000 volt.
Average error = ±0·0017 volt.

In Table II are given the potentials of a number of cells, showing the effect of varying the mercuric chloride concentration in solutions of hydrochloric acid of the following concentrations: 0·01, 0·1, 0·5, 1·0, 2·7, 4·6, 7·2, and 10·0N.

TABLE II.

Cell No.	[HCl].	[$HgCl_2$].	E_c.	π.	E.
		$[HCl] = 0{\cdot}01N$.			
1	0·0100	0·00013	0·2810	−0·0740	0·7958
2	0·0100	0·00119	0·3258	−0·0740	0·8406
3	0·0100	0·0154	0·3868	−0·0740	0·9016
4	0·0104	0·100	0·4671	−0·0734	0·9825
5	0·0100	0·150	0·4897	−0·0740	1·0045
		$[HCl] = 0{\cdot}10N$.			
6	0·0995	0·000256	0·1972	−0·0370	0·7490
7	0·100	0·0018	0·2385	−0·0370	0·7903
8	0·099	0·0103	0·2719	−0·0370	0·8237
9	0·106	0·0199	0·2912	−0·0360	0·8440
10	0·100	0·100	0·3603	−0·0370	0·9121
11	0·096	0·134	0·3735	−0·0375	0·9248
12	0·100	0·213	0·4082	−0·0370	0·9600
		$[HCl] = 0{\cdot}5N$.			
13	0·509	0·00057	0·1119	−0·0106	0·6901
14	0·508	0·00193	0·1347	−0·0106	0·7129
15	0·507	0·020	0·1842	−0·0106	0·7624
16	0·500	0·196	0·2750	−0·0106	0·8532
17	0·500	0·470	0·3329	−0·0106	0·9111

TABLE II (*contd.*).

Cell No.	[HCl].	[$HgCl_2$].	E_c.	π.	E.
		[HCl] = 1·0*N*.			
18	1·005	0·00053	0·0272	0	0·6160
19*	1·000	0·00099	0·0433	0	0·6321
20	1·050	0·00198	0·0564	+0·0008	0·6460
21	0·964	0·0196	0·1051	−0·0007	0·6932
22	0·960	0·0208	0·1080	−0·0008	0·6960
23	0·980	0·072	0·1543	−0·0004	0·7427
24	0·995	0·096	0·1616	0	0·7504
25	0·991	0·169	0·1911	0	0·7799
26	0·960	0·735	0·3000	−0·0008	0·8880
27	0·920	0·985	0·3207	−0·0014	0·9081
28	1·000	1·010	0·3292	0	0·9180
		[HCl] = 2·7*N*.			
29	2·73	0·0004	−0·0885	0·0257	0·5260
30	2·74	0·0024	−0·0526	0·0258	0·5620
31	2·74	0·0052	−0·0330	0·0258	0·5816
32	2·72	0·020	−0·0032	0·0256	0·6112
33	2·72	0·051	+0·0253	0·0256	0·6397
34	2·72	0·100	+0·0409	0·0256	0·6553
35	2·70	0·407	+0·1043	0·0250	0·7181
36	2·61	0·910	+0·1641	0·0240	0·7769
37	2·72	2·260	+0·2376	0·0256	0·8520
		[HCl] = 4·6*N*.			
38	4·68	0·0026	−0·1422	0·0469	0·4935
39	4·66	0·0032	−0·1355	0·0468	0·5001
40	4·67	0·021	−0·0825	0·0467	0·5530
41	4·62	0·024	−0·0791	0·0465	0·5562
42	4·53	0·192	−0·0160	0·0457	0·6185
43	4·63	0·529	+0·0238	0·0466	0·6592
44	4·44	0·966	+0·0480	0·0450	0·6818
45	4·60	1·033	+0·0543	0·0463	0·6894
46	4·60	3·80	+0·1494	0·0463	0·7845
		[HCl] = 7·2*N*.			
47	7·40	0·0028	−0·1994	0·0667	0·4561
48	7·30	0·0108	−0·1674	0·0680	0·4894
49	7·18	0·0961	−0·1082	0·0673	0·5479
50	7·40	0·977	−0·0322	0·0685	0·6251
51	7·20	3·80	+0·0318	0·0674	0·6880
		[HCl] = 10·0*N*.			
52	10·05	0·0039	−0·2374	0·0808	0·4322
53	10·19	0·0117	−0·2104	0·0815	0·4599
54	10·19	0·0986	−0·1518	0·0815	0·5185
55	10·05	0·937	−0·0836	0·0808	0·5860
56	10·00	3·80	−0·0314	0·0806	0·6380

* Cell No. 19 contained four electrodes, two of polished platinum foil and two of platinised platinum foil. They all gave identical results.

Variation of Potential with Concentration of Mercuric Chloride.—In Fig. 1 the potential of the oxidation element is plotted against the

logarithm of the mercuric chloride concentration, for each acid concentration. According to the equation:

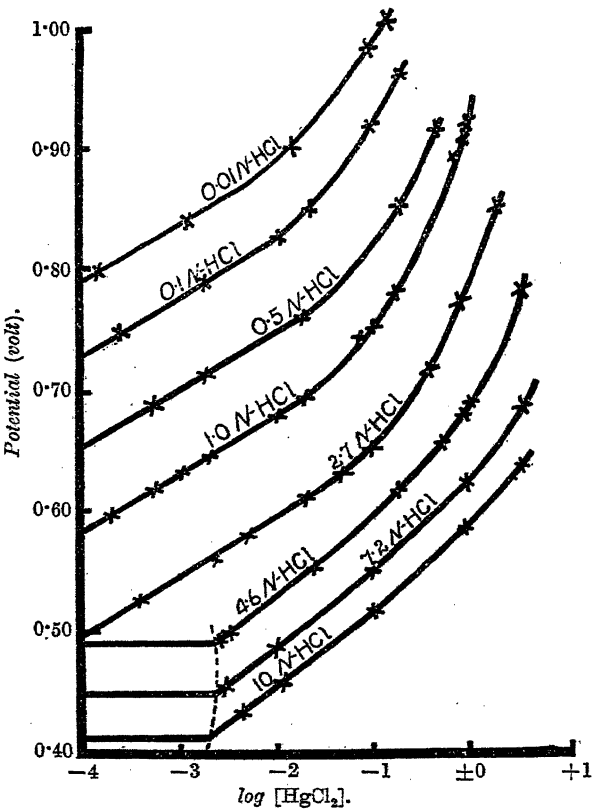
$$E = E_0 + 0{\cdot}029 \log [Hg^{\cdot\cdot}]^2/[Hg_2^{\cdot\cdot}] \quad . \quad . \quad . \quad (1)$$

since $$[Hg^{\cdot\cdot}] = k_2[HgCl_2]/[Cl']^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and $$[Hg_2^{\cdot\cdot}] = k_1/[Cl']^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

therefore $$E = E_0 + 0{\cdot}029 \log k_2^2[HgCl_2]^2/k_1[Cl']^2 \quad . \quad . \quad (4)$$

FIG. 1.



It follows that for a given acid concentration, the mercurous-ion concentration is constant, whilst the mercuric-ion concentration will be proportional to $[HgCl_2]$ since the feeble ionisation of mercuric chloride renders its contribution to the chlorine-ion concentration negligible.

Hence $$E = E_0' + 0{\cdot}058 \log [HgCl_2] \quad . \quad . \quad . \quad . \quad (5)$$

or the *E.M.F.* is a linear function of the logarithm of the mercuric chloride concentration.

From the graph, it will be seen that the logarithmic law holds in the more dilute solutions of mercuric chloride, but breaks down when the concentrations of mercuric chloride and hydrochloric acid are of the same order. It is noteworthy that in place of the theoretical slope of 0·058 volt for a ten-fold dilution, we obtained slopes of 0·060 volt in the 4·6*N*-, 7·2*N*-, and 10·0*N*-hydrochloric acid solutions, and of 0·047 volt in the lower acid concentrations. The discrepancy in the former case is not serious, but in the latter case is beyond the range of experimental error, and up to the present we have not been able to account for it.

To explain the deviations from the logarithmic law in the more concentrated mercuric chloride solutions, complex-ion formation may be assumed. Complex-ion formation between calomel and hydrochloric acid is unlikely, as calomel is known to form only a few double salts. Sherrill (*Z. physikal. Chem.*, 1903, **43**, 705; 1904, **47**, 103) and Noyes and Le Blanc (*Z. physikal. Chem.*, 1890, **6**, 389) have brought forward evidence in favour of the existence of the ion $HgCl_4''$, whilst Sand and Breest (*Z. physikal. Chem.*, 1907, **59**, 424) and Drucker (*Z. Elektrochem.*, 1912, **18**, 236) consider that the ion has the formula $HgCl_3'$. As the percentage of mercuric chloride in the form of complex ions is high, it may be seen from the equations $HgCl_2 + 2Cl' = HgCl_4''$ and $HgCl_2 + Cl' = HgCl_3'$ that when the mercuric chloride is present in the same concentration as the acid, a considerable decrease in the acid concentration must occur in order to allow the formation of these complex ions, and hence, according to equation (4), the potential of the cell will be increased. Quantitatively the behaviour of the system is given by equation (4) and an equation determining the equilibrium of the complex ion. According to Sherrill,

$$[HgCl_4'']/[HgCl_2][Cl']^2 = 70 \quad . \quad . \quad . \quad . \quad (6)$$

whilst according to Sand and Breest (if the value of the constant as recalculated by Drucker be used),

$$[HgCl_3']/[HgCl_2][Cl'] = 11{\cdot}5 \quad . \quad . \quad . \quad . \quad (7)$$

These two views have been reconciled by Linhart (*J. Amer. Chem. Soc.*, 1915, **37**, 258; 1916, **38**, 1272) who considers that both the ions $HgCl_3'$ and $HgCl_4''$ are present in solution [together with small quantities of polymerised mercuric chloride, $(HgCl_2)_2$, and the complex ions Hg_2Cl_5 and Hg_2Cl_6''], the equilibrium conditions being given by the equations:

$$[HgCl_3']/[HgCl_2][Cl'] = 9{\cdot}8 \quad . \quad . \quad . \quad . \quad (8)$$

$$[HgCl_4'']/[HgCl_3'][Cl'] = 4{\cdot}9 \quad . \quad . \quad . \quad . \quad (9)$$

and therefore $$[HgCl_4'']/[HgCl_2][Cl']^2 = 48 \quad . \quad . \quad . \quad . \quad (10)$$

From equation (9) it follows that in N-hydrochloric acid solution the complex ion $HgCl_4''$ is predominant, but in 0·01 N-acid solution the $HgCl_3'$ ion is the main constituent, whilst in 0·1N- and 0·5N-acid both ions are present in comparable amounts. We may therefore, as an approximation, apply equation (10) to solutions of mercuric chloride in N-hydrochloric acid. It is difficult to solve this equation to give the amounts of free unbound mercuric chloride in equilibrium with free acid and complex ion, but it is easy to proceed in the reverse manner. Thus, for any given total acid concentration [HCl], if an arbitrary value of the concentration of complex ion $[HgCl_4'']$ be assumed, it follows that the concentration of the free acid is $\{[HCl]-2[HgCl_4'']\}$, and hence the concentration of chlorine ion is $\{[HCl]-2[HgCl_4'']\}\gamma$, where γ is the activity coefficient corresponding with the concentration of the free hydrochloric acid. Hence by substitution in equation (6) we can determine the concentration of free mercuric chloride. The sum of free and combined mercuric chloride gives the total concentration of mercuric chloride, since that of the $Hg^{\cdot\cdot}$ and $HgCl^{\cdot}$ ions is negligible. The concentrations of free mercuric chloride and of chlorine ions may now be substituted in equation (4), together with the values of the constants $E = 1{\cdot}190$ volt, $k_1 = 3{\cdot}5 \times 10^{-18}$, and $k_2 = 10^{-14}$, to give a calculated value of the $E.M.F.$ corresponding with given values of [HCl] and total mercuric chloride.

Hence we obtain Table III, which gives the calculated values of the potential corresponding to different total concentrations of mercuric chloride in N-hydrochloric acid on the assumption that $HgCl_4''$ ions are formed.

TABLE III.

$[HCl] = 1{\cdot}0N$.

$[HgCl_4'']$.	Free [HCl].	γ.	[Cl'].	Free $[HgCl_2]$.	Total $[HgCl_2]$.	E (calc.).	E (obs.).
0·40	0·2	0·783	0·157	0·338	0·738	0·903	0·883
0·30	0·4	0·763	0·305	0·0672	0·367	0·846	0·825
0·10	0·8	0·796	0·637	0·00513	0·105	0·763	0·752
0·05	0·9	0·811	0·730	0·00195	0·0520	0·735	0·722
0·01	0·98	0·821	0·805	0·000322	0·0103	0·687	0·680

It will be seen that the considerable deviations from the logarithmic law that occur in concentrated solutions of mercuric chloride can be accounted for by assuming the existence of the ion $HgCl_4''$. If it is borne in mind that the values of k_1 and k_2 given above are strictly applicable only at 25° and not at 18°, that there are polymerised molecules $(HgCl_2)_2$, which give rise to Hg_2Cl_5' and Hg_2Cl_6'' ions, also present in solution, and moreover, that the formation of the complex ion $HgCl_4''$ causes a considerable reduction in the chlorine-ion concentration in the more concentrated mercuric chloride solutions,

which in turn favours the formation of $HgCl_3'$ ions, it will be seen that the method can only be expected to yield an approximation to the observed values of the potentials. However, the agreement is sufficient to show that the observed potentials can be accounted for on the basis of complex-ion formation.

Since in 0·1*N*- and 0·5*N*-hydrochloric acid both $HgCl_3'$ and $HgCl_4''$ ions are present to about the same extent, it is difficult to calculate the distribution of mercuric chloride between the various complex ions and to obtain calculated values of the potentials in these dilute acid solutions.

In the case of the three highest concentrations of acid, the portions of the curves parallel to the log $[HgCl_2]$ axis represent the potentials registered in solutions in which the mercuric chloride concentration is not high enough for equilibrium between Hg–Hg_2Cl_2–$HgCl_2$ to obtain. Under these conditions it was found that an oxidation potential was not registered, since it was independent of the mercuric chloride concentration, but a potential identical with the electrode potential of mercury and calomel described in the previous paper, and the data for the latter were used for plotting the horizontal portions of the curves. Such systems were found to be unstable since mercurous chloride decomposed into mercury and mercuric chloride until the concentration of the latter corresponded with the equilibrium value for the acid concentration under consideration.

Variation of Potential with Acid Concentration.—By drawing a line perpendicular to the abscissa and cutting it at the desired value of the mercuric chloride concentrations, we have read off from the curves in Fig. 1 the values of the potential of a cell in which the mercuric chloride concentration is constant and the hydrochloric acid concentration is varied between 0·01*N* and 10*N*. This has been done for five values of the former, namely, 1·0, 0·1, 0·01, 0·001, and 0·0001*N*. The results are in Table IV.

TABLE IV.

	$[HgCl_2]$, *M*.					
[HCl].	0·0001	0·001	0·01	0·1	1·0	4·0.
	Potential (volt).					
0·01	0·7910	0·8375	0·8885	0·9820	—	—
0·10	0·7295	0·7775	0·8260	0·9130	—	—
0·5	0·6530	0·7005	0·7475	0·8155	—	—
1·0	0·5840	0·6325	0·6795	0·7500	0·9110	—
2·7	0·4960	0·5455	0·5960	0·6550	0·7850	—
4·6	—	—	0·5305	0·5945	0·6860	0·7960
7·2	—	—	0·4890	0·5500	0·6240	0·6925
10·0	—	—	0·4560	0·5180	0·5875	0·6400

These results have been plotted in Fig. 2, which shows the relation between potential and hydrochloric acid concentration. This graph

also contains the curve of the electrode potential $2Hg$–$Hg_2^{\cdot\cdot}$ against acid concentration, based upon data given in the preceding paper.

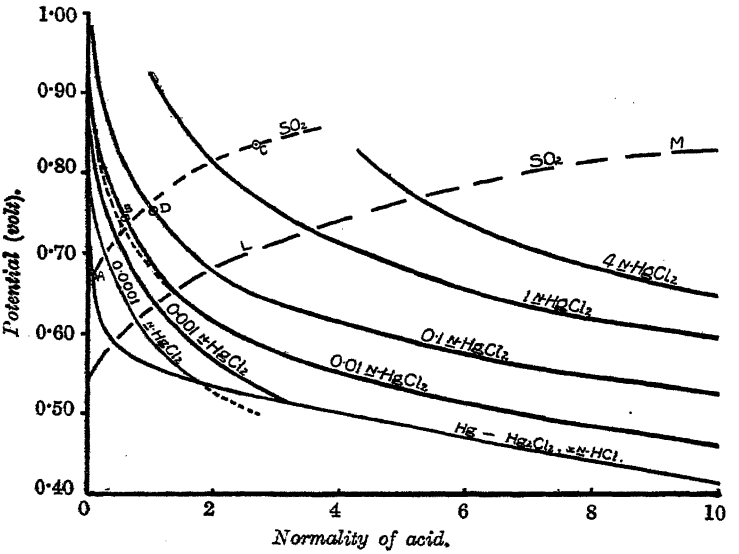
On the assumption that the ions $HgCl_3'$ and $HgCl_4''$ are formed according to equations (8) and (10), and since

$$[HgCl_4''] + [HgCl_3'] + [HgCl_2] = [HgCl_2]_{total}$$

then $$[HgCl_2]_{total} = [HgCl_2]\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}$$

or $$[HgCl_2] = [HgCl_2]_{total}/\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}.$$

FIG. 2.



Hence from equation (4)

$$E = E_0 + 0{\cdot}029 \log k_2^2/k_1 + 0{\cdot}058 \log [HgCl_2]_{total} / [Cl']\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}$$

or $$E = E_0 + 0{\cdot}029 \log k_2^2/k_1 + 0{\cdot}058 \log [HgCl_2]_{total} - 0{\cdot}058 \log [Cl']\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}.$$

In 0·01*M*-mercuric chloride, as the concentration of this salt is so low that the formation of these complex ions does not affect the concentration of acid appreciably, then for a constant value of $[HgCl_2]_{total}$ values of E corresponding to different concentrations of hydrochloric acid may be calculated.

In Fig. 2, the dotted curve indicates the potentials calculated in this manner, compared with the observed potentials, which are indicated by a continuous line. It is evident that good agreement has been obtained for concentrations of hydrochloric acid between 0·01*N* and 1·0*N*; for higher concentrations, however, the calculated

potentials decrease much more rapidly than the observed. It is difficult to account for this behaviour, partly because the activities of the different complex ions may vary in an unknown manner in concentrated acid solution, partly because the actual nature of these ions is unknown, and partly because the complex acids may not be completely dissociated. It may be pointed out, however, that in the most concentrated acid solutions the oxidation potential varies in the same way as the $Hg|Hg_2Cl_2,xN\text{-}HCl$ potential, *i.e.*, it is proportional to $-0{\cdot}058 \log [Cl']$, the chlorine-ion concentration being calculated on the basis of activity data. This indicates that the system is behaving as if complex-ion formation ceased in the high acid concentrations and as if it conformed to its normal behaviour according to equation (4). Although there is no theoretical reason for this supposition, it is interesting to notice that Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 385; compare preceding paper) found that the amount of mercuric chloride in equilibrium with mercury and calomel was independent of the acid concentration provided this was above $5N$. As almost all the mercuric chloride is present as complex ion, this is equivalent to saying that above $5N$-hydrochloric acid complex-ion formation is not increased by increasing the acid concentration.

The Action of Sulphur Dioxide on the Chlorides of Mercury.—In Fig. 2, we have indicated the variation of the oxidation–reduction potential of sulphur dioxide by the curve LM (Carter and James, J., 1924, **125**, 2234). Stewart and Wardlaw (*loc. cit.*) have studied the action of sulphur dioxide on the two chlorides of mercury, and in considering their results we have been guided by the principle that the system possessing the higher potential will oxidise the other system, being itself reduced.

The various reactions between mercury salts, hydrochloric acid, and sulphur dioxide were found to be extremely sensitive to small changes in acid concentration, and this is in agreement with the steepness of the potential curves, particularly in the region of low acid concentration.

(a) *Action of sulphur dioxide on calomel.* At 95°, Stewart and Wardlaw found that sulphur dioxide acted on calomel suspended in hydrochloric acid, in four ways, depending on the concentration of acid:

(1) $8N$- to $2N$-acid. Oxidation of calomel to mercuric chloride occurs, being complete only in the most concentrated acid and slight in $2N$-acid.

(2) $2N$- to $0{\cdot}16N$-acid. Decomposition of calomel and darkening of the solution, according to the equation: $Hg_2Cl_2 \longrightarrow Hg + HgCl_2$. We have confirmed the fact that this reaction is independent of the

sulphur dioxide; moreover, it ceases at approximately 0·16*N*-acid, because calomel could be boiled for several hours in 0·10*N*-acid without the slightest darkening.

(3) 0·16*N*- to 0·07*N*-acid. Inert region—calomel unaffected.

(4) 0·02*N*- to zero acid. Calomel is reduced to mercury by sulphur dioxide.

According to our graph, for acid concentrations between zero and 0·2*N*, the sulphur dioxide potential is lower than the $Hg–Hg_2Cl_2$ potential and hence reduction of the calomel is to be expected corresponding to (4).

Between 0·2*N*- and *N*-hydrochloric acid, it is to be expected that the oxidising action of sulphur dioxide on calomel will be slight, because the amount of mercuric chloride that must be formed to raise the oxidation potential as high as the sulphur dioxide potential is very small. Observation in this region is hindered by the fact that simultaneous decomposition of the calomel occurs into mercury and mercuric chloride. Above 2*N*-acid the oxidation of calomel becomes considerable and, according to our graph, should proceed almost to completion. It seems probable that equilibrium was not attained in all the experiments of Stewart and Wardlaw.

The point A on Fig. 2 represents the point on the $Hg–Hg_2Cl_2$ electrode potential curve (at 0·02*N*-HCl) where it intersects the sulphur dioxide curve.

(b) *Action of sulphur dioxide on mercuric chloride.* Stewart and Wardlaw found that if sulphur dioxide was passed for 12 hours through a solution of mercuric chloride in 0·48*N*-hydrochloric acid at 95°, calomel was formed, the amount decreasing with lowering of the mercuric chloride concentration, so that when $[HgCl_2] = 0·0094M$ the amount of calomel formed by reduction was very small. It therefore follows that the oxidation potential of sulphur dioxide in acid of this concentration is less than the oxidation of the mercury system when $[HgCl_2]$ is greater than 0·0094*M*, and greater than the oxidation potential when $[HgCl_2]$ is less than 0·0094*M*. This gives the point B in Fig. 2.

In 2·64*N*-hydrochloric acid, Stewart and Wardlaw found that mercuric chloride was not reduced until its concentration reached 1·92*M*. This gives the point C. In 1·0*N*-acid, the extent of reduction was very small when $[HgCl_2] = 0·1M$. This is the point D.

It will be seen that the line AC drawn through these four points gives a curve for the oxidation potential of sulphur dioxide which is similar in form to the curve LM based on direct potential measurements, but it is displaced upwards by about 0·2 volt. The discrepancy may be partly attributed to the different temperatures at

which our experiments and those of Stewart and Wardlaw were carried out, *viz.*, 18° and 95°, respectively.

Summary.

The conditions necessary for obtaining reproducible oxidation potentials of mercurous and mercuric chlorides in hydrochloric acid solution at 18° have been examined. The influence on potential of various concentrations of both the mercuric chloride and the hydrochloric acid has been determined over a wide range.

The departures from the logarithmic law that have been observed have been attributed to a large extent to the formation of complex ions.

Evidence has been adduced in favour of the existence of complex ions, especially $HgCl_4''$, in hydrochloric acid solutions of mercuric chloride.

The abnormal effect of hydrochloric acid stronger than 5*N* on the complex-ion formation, noticed by Richards and Archibald, has been confirmed.

The reactions of sulphur dioxide on the chlorides of mercury have been studied in the light of the electrochemistry of these systems.

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UNIVERSITY OF BIRMINGHAM,
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CCXLVIII.—*The Decomposition of Nitrous Acid in Aqueous Solution.*

By THOMAS WESTON JOHNS TAYLOR, ERNEST WILLIAM WIGNALL, and JOHN FREDERICK COWLEY.

THE decomposition of nitrous acid in aqueous solution is a complex phenomenon. The more important facts already known can be summarised as follows: (1) In contact with air, there is a certain amount of oxidation; if an inert gas replaces air, the reaction $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$ takes place (Montemartini, *Atti R. Accad. Lincei*, Rendiconti, 1890, **6**, ii, 263). (2) The rate of decomposition follows approximately a unimolecular law, in contact either with air (Ray, Dey, and Ghosh, J., 1917, **111**, 413) or with carbon dioxide (Montemartini, *loc. cit.*). (3) The rate is reduced by adding nitric oxide to the gas above the solution, and is slower

the greater the pressure of nitric oxide (Montemartini, *loc. cit.*; Klemenc and Pollak, *Z. physikal. Chem.*, 1922, **101**, 150). (4) The rate is much increased by bubbling an inert gas through the solution (Knox and Reid, *J. Soc. Chem. Ind.*, 1919, **38**, 105T) and apparently reaches no limit as the speed of bubbling is increased (Klemenc and Pollak, *loc. cit.*). (5) The reaction is reversible (Veley, *Chem. News*, 1892, **66**, 175), but the reverse reaction proceeds extremely slowly with dilute solutions of nitric acid (Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 375; 1901, **33**, 306).

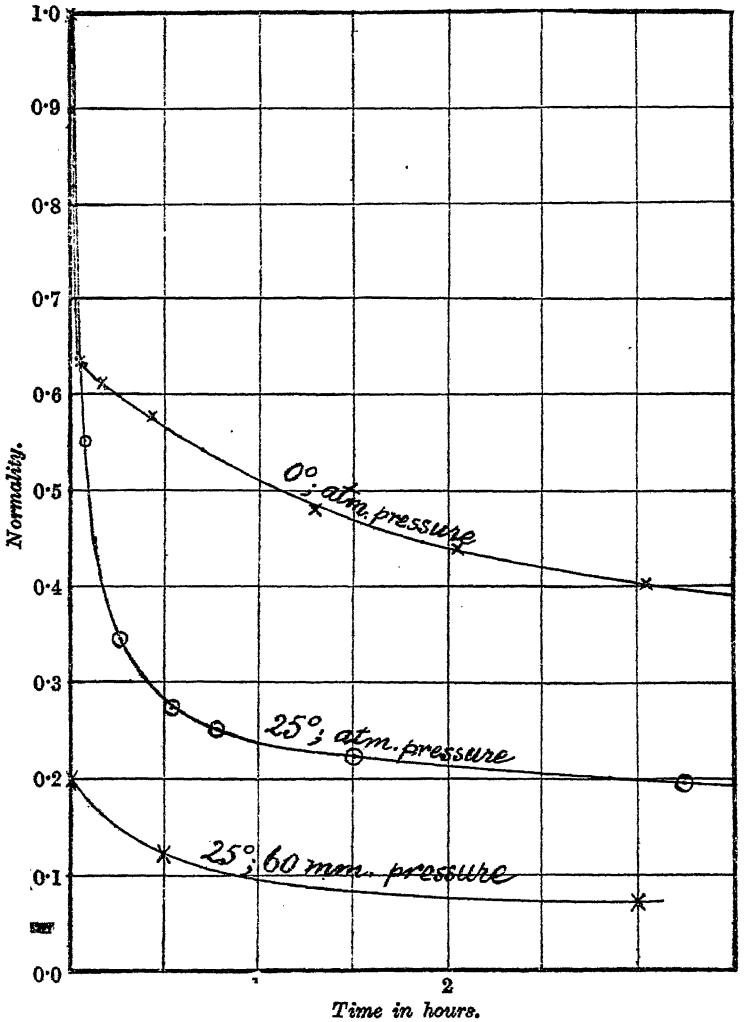
In an attempt to find conditions under which solutions of nitrous acid would be sufficiently stable for investigation of its reactions, the effect of reducing the area of surface of the solution in contact with the gas phase was tried. This can be done most simply by floating a layer of an immiscible liquid on the top of the solution; most liquids which might be used, however, such as benzene or ligroin, dissolve nitrogen trioxide from fairly strong solutions of nitrous acid, but the solubility of the trioxide is smaller in the mixture of higher paraffins sold as "medicinal paraffin," and this liquid has the added advantage that its high viscosity makes it possible to stir the lower aqueous layer without breaking up the paraffin layer.

Dilute solutions of nitrous acid prepared beneath a layer of this paraffin from a solution of pure barium nitrite (Witt and Ludwig, *Ber.*, 1903, **36**, 4384) and the equivalent of dilute sulphuric acid, and thus containing barium sulphate in suspension, are considerably more stable than similar solutions under nitrogen and very much more stable than those in contact with air. For example, equal volumes of a solution in identical vessels were kept at 25°, the one under paraffin and the other in contact with air; after 3 hours, the first showed 5% decomposition and the second 53%. Quite dilute solutions, *i.e.*, 0·1*N* and less, could be kept at 0° for 5 hours without the decomposition exceeding 4%. The solutions were stirred during these experiments by a small stirrer passing through the paraffin, but not at such a rate as to draw gas bubbles into the solution; the concentration of acid was determined by Veley's method (*Proc. Roy. Soc.*, 1893, *A*, **52**, 28).

When stronger solutions were investigated under paraffin, it was found that critical concentrations existed above which the rate of decomposition was very rapid and below which it was much slower. The critical concentration depends on the temperature, being higher the lower the temperature, and on the pressure of air above the paraffin, increasing with the pressure. Fig. 1 shows the rate of decomposition in two solutions, originally of *N* concentration, at 25° and at 0°, and also the effect at 25° of reducing to 60 mm. the pressure above a 0·2*N*-solution, *i.e.*, one which at atmospheric

pressure would decompose but slowly. Ray, Dey, and Ghosh (*loc. cit.*) noted this critical phenomenon and could not obtain a solution stronger than 0·185*N* which did not evolve nitric oxide rapidly when at 0° and in contact with air.

FIG. 1.



The velocity of the "slow" reaction at 25° was measured, and the results of any one experiment roughly agreed with the unimolecular law, although the velocity coefficient slowly decreased as the reaction proceeded; but the reaction is in no sense truly uni-

molecular—even well below the critical concentration the value of the velocity coefficient depends on the initial concentration and on the shape of the vessel in which the solution is kept, and thus has no absolute significance.

The velocity of the reaction under paraffin is also influenced by the presence of other substances in the solution; in 5*N*-sulphuric acid it is markedly smaller, and in 7*N*-acid smaller still. This result disagrees with that found by Klemenc and Pollak, who used solutions through which nitrogen was bubbling, but agrees with that of Knox and Reid (*loc. cit.*), whose solutions were in contact with air. The velocity is also much reduced by the presence of sodium sulphate, which at 0·65*M* concentration has an effect equivalent to 5*N*-sulphuric acid.

The presence of barium sulphate in suspension during these experiments had no appreciable influence on the stability of the acid, since similar experiments were carried out using nitrous acid prepared from pure sodium nitrite (Divers, J., 1899, **75**, 80) and sulphuric acid, and the rates of decomposition were those to be expected from the previous experiments, account being taken of the effect of the sodium sulphate.

These results show that, by using paraffin and sodium sulphate, solutions of nitrous acid the strengths of which do not exceed certain maximum values (0·4*N* at 0° and 0·2*N* at 25°, at atmospheric pressure) can be conveniently stabilised to a considerable extent. The complicated character of the decomposition has, however, not yet been satisfactorily explained. Klemenc and Pollak advance the improbable hypothesis that nitrous acid spontaneously breaks up into nitric oxide and the hydroxyl radical, and attribute its existence in solution to mutual action between molecules of the acid and of the solvent; they suggest that the rate of decomposition depends upon the rate of escape of nitric oxide from the solution. This, although accounting for the sensitiveness of a solution to its method of treatment, scarcely accounts for the sudden change in rate of decomposition shown in the figure.

The fact that the reaction is reversible does not come into play, because of the extremely slow rate of the reverse reaction at the dilutions investigated [see (5), p. 1924]. The critical phenomenon and its dependence on temperature and pressure must arise from the existence of some kind of equilibrium in which one of the substances involved is a gas of limited solubility in water; this equilibrium must be established with great rapidity to account for the observations of Klemenc and Pollak [(4), p. 1924].

The view advanced here is that in a solution of nitrous acid the equilibrium $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$ is set up, and that the com-

plicated nature of the decomposition arises from the behaviour of the anhydride; that this latter exists in solution is supported by the observations of Saposhnikov (*loc. cit.*) on the ease with which organic solvents will dissolve it from solutions of the acid. It is not the anhydride itself which escapes as gas from the solution, for, if this were so, the solution would contain eventually less nitric acid than the quantity corresponding to the equation of decomposition [(1), p. 1923], and experiment showed that in every case under paraffin the theoretical amount of nitric acid remained. If, however, the further equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$ tends to be set up in solution, the facts receive an intelligible explanation. In a completely stable solution, the concentration of water being assumed to be constant, the function $[NO][NO_2]/[HNO_2]^2$ would have a fixed value at any one temperature; but the concentration of nitric oxide cannot exceed a certain limit because of its slight solubility, and the limit will depend on the pressure. The existence of the "rapid" decomposition is accounted for. No completely stable solution, however, can exist, even in a sealed bulb where the pressure of nitric oxide can become high (Montemartini, *loc. cit.*), since the nitrogen peroxide is continually hydrated and removed from the equilibrium. During the "slow" decomposition two factors come into play: the rate of escape of nitric oxide and the rate of hydration of the peroxide. The concentration of the latter is probably extremely small and thus the quantity hydrated in unit time is small, and consequently the second factor under normal conditions is of less importance. Any factor tending to facilitate the escape of the nitric oxide, such as increased area of contact with the gas phase, addition of sand or charcoal (Frémy, *Compt. rend.*, 1870, **70**, 63), or reduction of pressure, will increase the rate of decomposition. The escape of a gas from solution has a rapid stage, followed by a slower stage (Perman, J., 1895, **67**, 868; Bohr, *Ann. Physik*, 1899, **68**, 507; Findlay and King, J., 1913, **103**, 1170) which follows a logarithmic law, thus agreeing with the behaviour of nitrous acid. The effect of added substances in reducing the rate of decomposition can be compared with the result found by Bohr that carbon dioxide escapes less rapidly from a solution of sodium chloride than from pure water.

Work is in progress on various reactions of nitrous acid stabilised in the manner described in this paper.

Our thanks are due to Dr. W. H. Mills for his helpful criticism and to Messrs. Brunner Mond & Co., Ltd., for their generosity in making a grant which has covered part of the expenses of this work.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, May 9th*, 1927.]

CCXLIX.—*The Action of the Metallic Derivatives of Ethyl Dehydroundecenoate upon Alkyl Halides.*

By WILLIAM WHALLEY MYDDLETON and RUDOLPH G. BERCHEM.

AN attempt to synthesise Δ^{10}-stearolic acid by acting upon the silver derivative of ethyl dehydroundecenoate with heptyl bromide in alcoholic solution resulted in the formation of silver bromide, ethyl heptyl ether, and free ethyl dehydroundecenoate. With the silver derivative in absence of alcohol, an excess of heptyl bromide gave silver bromide, heptene, and ethyl dehydroundecenoate. In each case, the yields of silver bromide and ethyl ester were practically quantitative.

n-Propyl, *iso*butyl and ethyl bromides and ethyl iodide were used in succession, and in each case quantitative yields of silver halide and ethyl dehydroundecenoate were obtained. Other products in these reactions were not investigated. The silver derivative obviously reacts with halogen acid derived from the alkyl halide.

During the preparation of the silver derivative by the action of alcoholic silver nitrate upon the ester, we followed the reaction more closely than Krafft (*Ber.*, 1896, **29**, 2232) and found the yields of silver derivative and free nitric acid required for the equation:

$$CH{:}C\cdot[CH_2]_8\cdot CO_2Et + 2AgNO_3 = AgNO_3,CAg{:}C\cdot[CH_2]_8\cdot CO_2Et + HNO_3.$$

We add to Krafft's observations that the silver derivative is soluble in hot alcohol and is stable in bright sunlight. The presence of a little free dehydroundecenoic acid in the ester results in the formation of a grey silver derivative which rapidly darkens in daylight.

Sodium derivatives of acetylenic compounds are not so readily prepared as the silver derivatives, but by the action of finely powdered sodamide upon ethyl dehydroundecenoate in toluene we obtained the sodium derivative of dehydroundecenoamide. The action of this compound upon alkyl halides was similar to that of the silver derivative.

EXPERIMENTAL.

Bromination of Undecenoic Acid.—Light petroleum (b. p. 60—80°) was treated with a slight excess of bromine, washed after some time with sodium bisulphite solution and with water, dried, and distilled. To a solution of 170 g. of undecenoic acid (m. p.

24·5°; b. p. 168·3°/15 mm.) in 500 c.c. of the solvent, cooled in a freezing mixture, 150 g. of bromine were added during 1½ hours with efficient stirring. After 1 hour the precipitate was filtered off, washed with 100 c.c. of cold solvent, and dried (250 g.; m. p. 38·5°). The remainder of the dibromo-acid was obtained as an oil after washing the filtrate with a solution of sodium bisulphite and then with water and drying and evaporating the solvent. The yield of oil was practically the same in a number of brominations (Found: Br, 46·2; equiv., by titration with alkali, 345·1. Calc. for $C_{11}H_{20}O_2Br_2$: Br, 46·5%; equiv., 344·0).

Preparation of Ethyl Dehydroundecenoate and its Silver Derivative.—Dehydroundecenoic acid was prepared from the dibromo-acid by Krafft's method (*loc. cit.*) and esterified with lime-dried alcohol and concentrated sulphuric acid. The ester had b. p. 145°/15 mm.

(*a*) A solution of 2 g. of the ethyl ester in 5 c.c. of absolute alcohol was added to 3·24 g. of silver nitrate in 105 c.c. of alcohol; 4·7 g. of the silver derivative were obtained. The filtrate and washings (10 c.c.) were shaken with solid potassium chloride and filtered. The filtrate required for neutralisation 9·0 c.c. of *N*-sodium hydroxide.

(*b*) 17·5 G. of the ester, 28·4 g. of silver nitrate, and 1 l. of alcohol gave 38·5 g. of the silver derivative, and the filtrate required 82·1 c.c. of *N*-alkali (Found: Ag, 44·5. Calc. for $C_{13}H_{21}O_2Ag,AgNO_3$: Ag, 44·3%).

Action of the Silver Derivative upon Heptyl Bromide in Alcohol.—The silver derivative precipitated from 17·5 g. of the ester was washed and dissolved in 300 c.c. of warm alcohol, 30 g. of heptyl bromide were added, and the solution was warmed under reflux on the water-bath; 30 g. of silver bromide separated during 3 hours. Alcohol was distilled from the filtered solution, and the residue fractionated.

Fraction (*a*), boiling below 140°/15 mm., was redistilled and collected up to 168°/760 mm. After it had been warmed with aqueous caustic potash to hydrolyse heptyl bromide and extracted with ether, an oil was obtained. Heptyl alcohol was removed from this by treatment with successive quantities of sodium. The remaining liquid was distilled and collected at 165—166°/760 mm. (3·5 g.) (Found: C, 74·65; H, 13·7. Calc. for $C_7H_{15}\cdot O\cdot C_2H_5$: C, 74·9; H, 14·0%).

Fraction (*b*) (16 g.), collected at 145°/15 mm., was ethyl dehydroundecenoate, since it gave after hydrolysis an acid of m. p. 43—44° (Found: C, 72·3; H, 10·2; equiv., by titration, 185·2. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 10·0%; equiv., 182·1).

Action of the Silver Derivative upon Heptyl Bromide in Absence of Alcohol.—The silver derivative from 15 g. of the ester was dried in a

vacuum desiccator during 2 days and then warmed with 50 g. of heptyl bromide on the water-bath, the flask being shaded. The cooled solution was filtered after dilution with ether. The filtrate gave a fraction, b. p. 95—100°/760 mm. On redistilling this, 4·5 g. were collected at 96—98°. Bromine in the cold converted this into an oil, b. p. 105—107°/15 mm. αβ-Dibromoheptane has b. p. 105—107°/15 mm. (Found: Br, 61·5. Calc. for $C_7H_{14}Br_2$: Br, 62·0%).

Formation of the Sodium Derivative.—Ethyl dehydroundecenoate was heated under reflux for about 2 days with toluene in which a 5% excess of finely powdered sodamide was suspended; ammonia was slowly evolved. The flocculent precipitate of the sodium derivative of dehydroundecenoamide was treated with excess of heptyl bromide. Sodium bromide was slowly formed and the filtered solution gave practically the whole of the ethyl dehydroundecenoate.

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BIRKBECK COLLEGE,
UNIVERSITY OF LONDON. [*Received, April 10th,* 1927.]

CCL.—*Besson's Supposed Phosphorus Suboxide,* P_2O.

By LESLIE JAMES CHALK and JAMES RIDDICK PARTINGTON.

BESSON describes (*Compt. rend.*, 1897, **124**, 763; 1897, **125**, 1032; 1901, **132**, 1556; compare *Bull. Soc. chim.*, 1900, **23**, 582) the preparation of an oxide, P_2O, (i) by heating phosphoryl chloride with phosphonium bromide, (ii) by the action of a slow stream of air on a solution of phosphorus in carbon tetrachloride, and (iii) by heating a concentrated solution of phosphorous acid with phosphorus trichloride. The identical products are stated to be yellowish-red and stable at 100°, but decomposed in a vacuum at 135° with the evolution of oxygen. Analysis gave about 79% of phosphorus (P_2O requires 79·49%). The substances obtained by Michaelis and Pitsch (*Ber.*, 1899, **32**, 337; *Annalen*, 1900, **310**, 45) by the action of hydrochloric acid on a solution of yellow phosphorus in aqueous-alcoholic potassium hydroxide, and by the action of acetic anhydride on a solution of hypophosphorous acid in glacial acetic acid, were considered by Besson to be largely P_2O contaminated by phosphorus and solid hydrogen phosphide.

Preparation of Besson's Oxide.—10 G. of Kahlbaum's phosphorous

acid were dissolved in 8 g. of water in a flask under a reflux condenser and 50 g. of phosphorus trichloride were added. Hydrogen chloride was steadily evolved and crystals were formed. These consisted of phosphorous acid, and not phosphorus trioxide, as required by the equations given by Besson, *viz.*, $PCl_3 + H_3PO_3 = 3HCl + P_2O_3$, followed by $2P_2O_3 = P_2O + P_2O_5$. On heating for about 15 minutes on a water-bath with shaking, the crystals disappeared and a yellow solid began to separate. On further heating, red particles appeared. A viscous layer settled out which contained most of the deposit, the upper layer being unchanged phosphorus trichloride. Reaction is complete in 6 hours. Besson states that a substance with the appearance of phosphorus pentoxide is formed in the reaction, but this could not be confirmed, neither was a hissing noise observed on adding water to the residue, although heat was evolved by the action of water on unchanged trichloride—if the upper layer is poured off before the addition of water there is practically no evolution of heat.

The product was filtered, washed with cold water according to the directions of Besson, and dried in a vacuum over phosphorus pentoxide for 3 weeks. The filtrate contained phosphorous, phosphoric, and hydrochloric acids, most of the phosphorus being in the form of phosphorous acid. The dry powder was yellowish-red, but contained darker red particles, and was free from chlorine. The yield from 10 g. of phosphorous acid was 0·7 g. In this way, the preparations numbered I, II, III, and VII in the tables were obtained.

Action of Phosphorus Trichloride on Crystalline Phosphorous Acid.—Although the preceding experiment was performed exactly as specified by Besson, it was clear that it would be better to use crystalline phosphorous acid instead of the solution. 50 G. of phosphorus trichloride and 10 g. of solid phosphorous acid did not react until the mixture was warmed; the acid then dissolved completely and a yellow solid soon appeared. This turned redder on further heating for 5 or 6 hours, and the product was then isolated and dried as before. It was exactly similar in appearance to the previous product. The liquid poured off from the solid was mainly unchanged trichloride (43 g.). The yield of "oxide" was about the same as in the first method. The preparations numbered IV, V, VI, and VIII were obtained by this method. Preparation V, containing 86·7% of phosphorus, was not further examined.

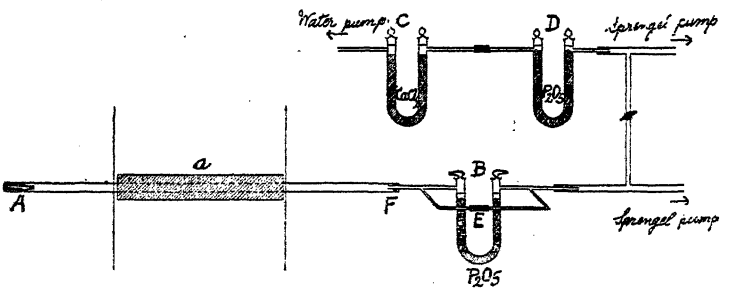
The Action of Phosphorus Trichloride on Phosphorous Acid below 70°.—50 G. of phosphorus trichloride and 10 g. of phosphorous acid were heated so that the temperature never rose beyond 70°. The action was slow, but no further yield appeared after 20 hours. Only 0·15 g. of product resulted, which was pure yellow without any tinge

of orange, and appeared homogeneous under the microscope. The washings contained phosphorous acid and a small amount of phosphoric acid, but no hypophosphorous acid. The upper layer yielded 33·5 g. of unchanged trichloride. The dry powder, specimen IX, had a stronger odour of phosphine than that prepared at 100°.

Analysis of the Products.—The preparations were analysed by the method described by Chapman and Lidbury (J., 1899, **75**, 973), except that phosphoric acid was estimated by the method described by Treadwell (" Quantitative Analysis," p. 437).

The water and hydrogen contents of the preparations were determined by a modification of the apparatus described by Burgess and Chapman (J., 1901, **79**, 1235), which is shown in Fig. 1. The aluminium foil used by these experimenters was omitted. The substance was weighed into a small tube, A, which was introduced

FIG. 1.



into the Bohemian-glass tube, F, 9 mm. in diameter and 120 cm. long. The part inside the resistance furnace, *a*, contained a roll of bright copper gauze. The whole apparatus was first thoroughly cleaned and dried by prolonged heating in a vacuum. The junction with the phosphorus pentoxide absorption tube, B, was made with sealing wax, since this part remained quite cool, so that the tube B could be removed easily for weighing. A screw-clip on the pressure tubing, E, enabled the tube B to be evacuated independently of the tube AF. The substance in A darkened on heating and evolved gas, which was collected in the receiver of the Sprengel pump exhausting the apparatus. When no further gas collected and a vacuum was re-established, the apparatus was allowed to cool and disconnected, and the tubes A and B were weighed. The tube A contained a dark grey residue, sometimes containing white, opaque specks, which were not glassy. Practically the whole of the phosphorus content of this residue could be extracted by boiling water, but the undissolved residue was in every case analysed for phosphorus.

When the preparations were heated with water in a sealed tube for 8 hours at 100°, and the tube was opened under mercury, only a very small diminution in volume was noticed, and the solution was found to contain phosphorous, but not hypophosphorous, acid. Besson attributed the production of phosphorous acid in this experiment to oxidation of P_2O: $P_2O + O_2 + 3H_2O = 2H_3PO_3$, the absorption of oxygen being inferred from a diminution of pressure; he also noticed a smell of phosphine. We find no such diminution of pressure, and there can be no doubt from this and from the quantitative experiments described below that the phosphorous acid is present as such in the original preparations. On further heating the residue from this experiment with water, more phosphorous acid was obtained, but in diminished amount, and an adsorption phenomenon is indicated. The presence of uncombined water in the preparations is considered improbable, since a portion of preparation III, on being kept in a vacuum over phosphorus pentoxide for 2 months, gave practically the same results for water and hydrogen on distillation (0·1 g. gave 0·0142 g. of residue with 43% P, 2·2 c.c. of hydrogen and 0·0056 g. of H_2O) as the freshly dried preparation. The probable constituents of the preparations are therefore: free phosphorus, phosphorous acid, and solid hydrogen phosphides. The preparation made below 70° may be expected to contain more solid phosphides, since a slow reaction between phosphorus trichloride and phosphorous acid in the cold is said to give these substances, whilst at higher temperatures (170°) red phosphorus is said to be the only product.

We assume that the only primary constituents of the preparations are phosphorous acid and phosphorus, the amount of the former being directly estimated from the phosphoric acid in the residue left after distillation in a vacuum. The weight of water and the volume of hydrogen obtained on distillation in vacuum can then be compared with those calculated from the equation: $8H_3PO_3 = 3P_2O_5 + 9H_2O + 2P + 3H_2$. The phosphorus content of the residue was generally above 40%, whereas that of metaphosphoric acid is 38·8% and that of phosphorus pentoxide 43·7%. That the residue should consist mainly of phosphorus pentoxide rather than metaphosphoric acid might appear improbable, but the pentoxide may be produced by the prolonged heating in vacuum of free phosphorus and metaphosphoric acid: $10HPO_3 + 2P = 6P_2O_5 + 5H_2$. The results of the distillation experiments, as is seen from Table I, are in agreement with this hypothesis, except that the hydrogen obtained from the oxide prepared below 70° was greater than the calculated amount, a result which would be expected if solid hydrogen phosphides are present. In other cases, the hydrogen calculated is only slightly

lower than the experimental value, which may indicate the presence of a little solid hydrogen phosphide (compare Burgess and Chapman, *loc. cit.*). The dark colour of the residue obtained on heating in a vacuum is probably due to a trace of free carbon derived from organic matter introduced from the cork of the flask in the preparation of the "oxide." This was estimated by difference on the assumption that the remainder of the residue was phosphorus pentoxide, and it was always very small.

In all cases the gas collected from 0·1 g. of preparation was 2—4 c.c. It was shown to be hydrogen by explosion with oxygen. No contraction was observed with the gas, before or after explosion, in contact with dilute acid or alkali. The contraction on explosion was slightly less than the calculated, although no gas except hydrogen could be detected by qualitative tests. The alleged evolution of oxygen on heating the substance was negatived by experiments in which the copper gauze was omitted. The gas collected in this case was phosphine; it suffered no contraction in contact with alkaline pyrogallol, and on explosion with oxygen gave white fumes of phosphoric acid. The phosphorus contents of the various preparations were as follows :

Preparation.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
%P.	85·1	86·0	86·8	81·1	86·7	86·2	88·8	88·2	87·6

These results definitely exclude the composition P_2O.

In Table I, column 2 gives the actual amount of oxide used in the analysis. The figures in the remaining columns, however, have been calculated to 0·1 g. of oxide for the purpose of comparison. This applies also to all the figures in Tables II and III.

TABLE I.

Effect of distillation of the preparations.

Prep. No.	Weight (g.).	Residue (g.).	H_2O (g.).	Gas (c.c.).	H_2 (c.c.).	H_2O (calc.) (g.).	H_2 (calc.) (c.c.).
I	0·0950	0·0160	0·0059	2·8	2·6	0·0054	2·2
II	0·1081	0·0155	0·0065	3·0	2·9	0·0057	2·4
III	0·1060	0·0135	0·0051	2·2	2·0	0·0050	2·1
IV	0·0987	0·0176	0·0074	3·5	3·2	0·0064	2·7
VI	0·0945	0·0149	0·0063	2·5	2·5	0·0054	2·3
VII	0·0993	0·0121	0·0050	1·7	1·5	0·0044	1·8
VIII	0·1058	0·0128	0·0055	2·1	1·9	0·0047	2·0
IX	0·0595	0·0116	0·0044	4·6	4·4	0·0034	1·4

Specimen IV still contained phosphorous acid which could be extracted by washing. Specimens VII and VIII were washed for a longer time than the others and the phosphorus content is higher, indicating a more complete removal of phosphorous acid. Only 0·0595 g. of Specimen IX was available for distillation.

Table II contains the analyses of the residues left after distillation. Except in the cases of Preparations I and IX, all the phosphorus (as phosphoric acid) was extracted by boiling water. In these two cases, the residues after extraction contained 0·0010 g. and 0·0008 g. of free phosphorus, respectively (compare Burgess and Chapman, *loc. cit.*). The fifth column gives the amount of phosphorous acid equivalent to the phosphorus contained in the residue as P_2O_5, the sixth the amounts of hydrogen and oxygen equivalent to this, *viz.*, $(H_3PO_3)\times(51/82)$. The last column contains the sum of the weights of phosphorus, hydrogen, carbon, and oxygen in 0·1 g. of preparation, *i.e.*, the sum of the figures in columns 4, 6, and 7, and is equal to 0·1 to within 2%. This supports the hypothesis that the supposed oxide P_2O contains free phosphorus and phosphorous acid only.

TABLE II.

Composition of residue after distillation.

Prep. No.	Weight g.	% P in residue.	C. (calc.).	H_3PO_3 equiv. to P extracted.	H and O as H_3PO_3.	P in 0·1 g. "oxide."	Total.
I	0·0160	38·4	0·0009	0·0217	0·0135	0·0851	0·0995
II	0·0155	42·0	0·0005	0·0230	0·0143	0·0860	0·1008
III	0·0135	42·2	0·0006	0·0201	0·0125	0·0868	0·0999
IV	0·0176	42·0	0·0007	0·0261	0·0162	0·0811	0·0980
VI	0·0149	42·2	0·0005	0·0222	0·0138	0·0862	0·1005
VII	0·0121	41·5	0·0006	0·0177	0·0110	0·0888	0·1004
VIII	0·0128	42·5	0·0004	0·0192	0·0119	0·0882	0·1005
IX	0·0116	37·2	0·0009	0·0139	0·0086	0·0876	0·0971

The percentage of phosphorus in Preparations VII and VIII corresponds very nearly with that in the supposed suboxide P_4O, but the behaviour on distillation in a vacuum is different. Burgess and Chapman (*loc. cit.*) found that 0·1 g. of the supposed P_4O gave on distillation about 10 c.c. of hydrogen and left practically no residue, whereas these preparations give only 1—3 c.c. of hydrogen and leave 12% of residue. Burgess and Chapman, however, decomposed the water vapour by heated aluminium.

From the experimentally determined values of phosphorus, oxygen, and hydrogen in the supposed oxide, a formula for the latter may be calculated. This is done in Table III, in which the total should be 0·1 g. This is seen to be the case within 2%. The oxygen is calculated on the assumption that the phosphorus extracted by hot water from the residue after distillation existed as pentoxide.

The properties of the supposed oxide are similar to those of scarlet amorphous phosphorus and of the supposed solid hydrogen phosphides. It is insoluble in water, alcohol, benzene, chloroform, or ether. Dilute nitric acid dissolves it at 40°, whilst concentrated nitric acid causes inflammation. Hydrogen peroxide and sodium

TABLE III.

Prep. No.	P (obs.).	H_2O (obs.).	O (calc.).	H (obs.).	C (obs.).	Total.	Formula.
I	0·0851	0·0059	0·0079	0·0002	0·0009	0·1000	$P_2O_{0·59}H_{0·65}$
II	0·0860	0·0065	0·0084	0·0003	0·0005	0·1017	$P_2O_{0·64}H_{0·70}$
III	0·0868	0·0051	0·0073	0·0002	0·0006	0·1000	$P_2O_{0·53}H_{0·53}$
IV	0·0811	0·0074	0·0095	0·0003	0·0007	0·0990	$P_2O_{0·77}H_{0·68}$
VI	0·0862	0·0063	0·0081	0·0002	0·0005	0·1013	$P_2O_{0·62}H_{0·67}$
VII	0·0888	0·0050	0·0065	0·0001	0·0006	0·1010	$P_2O_{0·48}H_{0·48}$
VIII	0·0882	0·0055	0·0070	0·0002	0·0004	0·1013	$P_2O_{0·52}H_{0·55}$
IX	0·0876	0·0044	0·0056	0·0004	0·0009	0·0989	$P_2O_{0·42}H_{0·63}$

hypochlorite solution oxidise it to colourless solutions containing phosphoric acid. Concentrated ammonia turns it slightly darker in colour, the original colour being restored by exposure to air or by the action of acids. Alcoholic potassium hydroxide forms a dark red solution with evolution of phosphine, the solution being similar to that formed by the supposed suboxide P_4O (as was found by trial).

The mechanism of the formation of Besson's substance (which is really of variable composition) is probably as follows. The phosphorous acid may be decomposed with evolution of phosphine. The latter is known to react with phosphorus trichloride giving, according to the conditions, solid hydrogen phosphide or phosphorus. When prepared at lower temperatures, the product may contain appreciable amounts of solid hydrogen phosphide. It is also possible that phosphorus trioxide may be formed by the action of the trichloride on phosphorous acid (Abegg, "Handbuch," III, iii, 420; the reference to Krafft and Neumann, *Ber.*, 1901, **34**, 566, there given does not appear to be relevant). The trioxide might then decompose, either alone or by interaction with phosphorus trichloride, to form phosphorus or solid hydrogen phosphides.

Summary.

The supposed oxide of phosphorus, P_2O, formed by the action of phosphorus trichloride on phosphorous acid under the conditions described by Besson has neither the composition nor properties attributed to it by that investigator. It is somewhat variable in composition and appears to be a mixture of finely divided amorphous phosphorus with strongly adsorbed phosphorous acid, although, especially when prepared at lower temperatures, solid hydrogen phosphides may be present. The amount of oxygen present is always much less than is required by the formula P_2O, and hydrogen also is always present, even after prolonged drying over phosphorus pentoxide.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

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CCLI.—*Syntheses of Glucosides. Part I. The Synthesis of Indican.*

By ALEXANDER ROBERTSON.

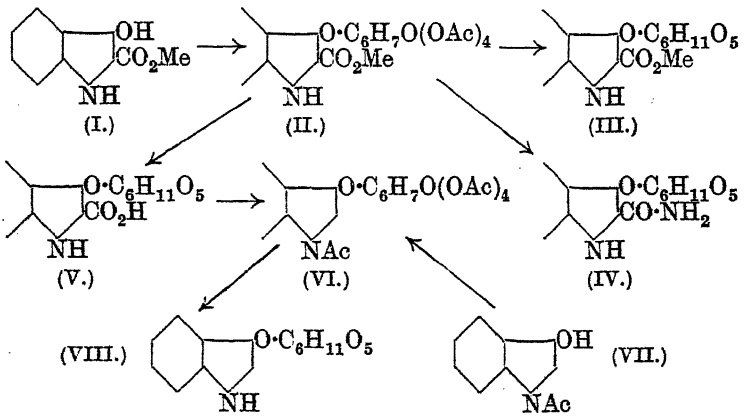
THE glucoside indican, 3-β-glucosidoxyindole, was first isolated by Schunk (*Phil. Mag.*, 1855, **10**, 74; 1858, **15**, 127) from *Polygonum tinctorium*, who stated that the indigotin-yielding substance in *Isatis tinctoria*, "woad," was the same. It was, however, not until many years afterwards that its correct formula was indicated by Marchlewski and Radcliffe (*J. Soc. Chem. Ind.*, 1898, **17**, 434), who suggested that the glucoside had possibly the formula $C_{14}H_{17}O_6N$, and that, on hydrolysis, glucose and indoxyl were formed, the latter on oxidation being converted into indigotin. The proof that indican is an indoxyl glucoside, and that the sugar obtained from it is glucose, was supplied by Hazewinkel (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 512). About the same time, Hoogenwerff and ter Meulen (*ibid.*, p. 520) isolated the glucoside in a crystalline condition from *Polygonum tinctorium* and *Indigofera leptostachya*. They showed that it had the formula $C_{14}H_{17}O_6N$ and when crystallised from water contained $3H_2O$. By hydrolysis of the glucoside in the presence of air, they obtained slightly impure indigotin; and later the identity of the sugar with *d*-glucose was indicated by ter Meulen (*Rec. trav. chim.*, 1905, **24**, 444). Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 101) showed that the glucoside in *Polygonum tinctorium* is not the same as the indigo-yielding substance in *Isatis tinctoria* as claimed by Schunk, and also that indican was slowly hydrolysed by emulsin, as well as by its specific enzyme, indemulsin.

Perkin and Bloxam (J., 1907, **91**, 1715), Perkin and Thomas (J., 1909, **95**, 793), and Thomas, Bloxam, and Perkin (J., 1909, **95**, 824), working with improved methods, isolated the crystalline glucoside from *Indigofera leptostachya*, *I. sumatrana*, *I. arrecta*, and *Polygonum tinctorium*, and confirmed in detail the work of Hoogenwerff and ter Meulen, Hazewinkel, and Beyerinck. In addition, these workers obtained the glucoside in the anhydrous state. From a study of the hydrolysis of methylated indican, Macbeth and Pryde (J., 1922, **121**, 1660) showed that the glucoside is in all probability a normal β-derivative. This is in agreement with the conclusions arrived at by ter Meulen (*loc. cit.*) as a result of a study of the hydrolysis of the glucoside by enzymes.

In attempting the synthesis of indican, the most obvious method was to obtain the penta-acetyl derivative by the interaction of 1-acetyl-3-hydroxyindole and tetra-acetyl-α-glucosidyl bromide in

acetone solution in the presence of aqueous alkali. Reference to the literature indicated the difficulty of preparing a sufficient quantity of the acetylhydroxyindole, and the instability of the latter in the presence of alkali. Accordingly, another method for the synthesis of the glucoside was devised.

Methyl 3-O-*tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate* (II) was obtained in good yield by the interaction of methyl 3-hydroxyindole-2-carboxylate (I) and tetra-acetyl-α-glucosidyl bromide in acetone solution in the presence of potassium hydroxide.



This penta-acetyl glucoside on hydrolysis with methyl-alcoholic potash yielded 3-β-*glucosidoxyindole*-2-*carboxylic acid* (V), which was conveniently isolated from the reaction mixture as the potassium salt. The latter, when treated with fused sodium acetate and acetic anhydride, first on the water-bath and then at 160°, was acetylated and the carboxyl group simultaneously eliminated with the formation of 1-*acetyl*-3-O-*tetra-acetyl*-β-*glucosidoxyindole* (VI). In order to verify the constitution of this substance, a small quantity of it was prepared directly by the interaction of 1-acetyl-3-hydroxyindole (VII) (D.R.-P. 108761) and tetra-acetyl-α-glucosidyl bromide in a cooled acetone solution in the presence of potassium hydroxide. The specimens of *penta-acetylindican* thus obtained were identical. The penta-acetyl glucoside was deacetylated with methyl-alcoholic ammonia, and 3-β-*glucosidoxyindole*, indican (VIII), obtained in good yield. The properties of the synthetic glucoside were identical with those of the natural product described in detail by Perkin and his collaborators (*loc. cit.*).

Hydrolysis of the synthetic indican under various conditions gave the same products as those obtained by these authors, by Hazewinkel (*loc. cit.*) and by Beyerinck (*loc. cit.*).

On deacetylation of the glucoside (II), a mixture of *methyl* 3-β-*glucosidoxyindole*-2-*carboxylate* (III) and 3-β-*glucosidoxyindole*-2-*carboxylamide* (IV) was obtained, but the latter could not be isolated in a crystalline condition. Hydrolysis and acetylation, however, established the nature of the uncrystallised syrup.

The preparation of methyl 3-hydroxyindole-2-carboxylate (Vorländer, *Annalen*, 1898, **301**, 349) was carried out by the method described for the preparation of the corresponding ethyl ester (D.R.-P. 105495). This methyl ester on acetylation yielded an O-*acetyl* derivative.

EXPERIMENTAL.

Methyl 3-*Hydroxyindole*-2-*carboxylate* (I). — To pulverised sodium (2·7 g.) and methyl phenylglycine-*o*-carboxylate (25 g.) in benzene (100 c.c.), one drop of anhydrous methyl alcohol was added and the mixture was gently warmed on the steam-bath until a vigorous reaction set in; the sodium derivative of methyl 3-hydroxyindole-2-carboxylate was then deposited as a solid. When this reaction had almost ceased, the mixture was heated under reflux for 30 minutes and then cooled. The sodium derivative was collected, washed with benzene, dried, and dissolved in ice-water (250 c.c.), and the solution was filtered after treatment with charcoal and acidified with acetic acid (50%). The indoxylic ester thus precipitated crystallised from methyl alcohol (70%) (charcoal) in elongated, glistening needles, m. p. 157—158°. Yield, 15 g.

Methyl 3-*acetoxyindole*-2-*carboxylate* was obtained in almost theoretical yield when methyl 3-hydroxyindole-2-carboxylate (2 g.), fused sodium acetate (2 g.), and acetic anhydride (10 c.c.) were heated under reflux for 1 hour. Water was added to the cooled mixture, and the *acetyl* derivative gradually crystallised. After recrystallisation from methyl alcohol (50%) and then from benzene–ligroin (1 : 9), it was obtained in glistening, elongated prisms, m. p. 145° (Found: C, 62·1; H, 4·7. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7%). It is insoluble in dilute alkali solution. Attempts to obtain a diacetyl derivative were unsuccessful.

Methyl 3-*Tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate* (II).—A cooled solution of potassium hydroxide (2·8 g.) in water (20 c.c.) was gradually added to one of methyl 3-hydroxyindole-2-carboxylate (9·3 g.) and tetra-acetyl-α-glucosidyl bromide (20·5 g.) in pure acetone (90 c.c.) cooled to 10°; the acetyl glucoside soon began to crystallise. After remaining at room temperature for 4 hours, the mixture was diluted with water (50 c.c.) and cooled in ice, and the solid was collected and recrystallised from hot methyl alcohol (charcoal). The *acetyl glucoside* was thus obtained in colourless

prisms with blunt ends, m. p. 229—230° (Found: C, 55·5; H, 5·2. $C_{24}H_{27}O_{12}N$ requires C, 55·5; H, 5·2%). Yield, 16·5 g.

This glucoside is sparingly soluble in ether and in cold alcohol, and moderately easily soluble in hot alcohol. A penta-acetyl derivative could not be obtained.

3-β-*Glucosidoxyindole-2-carboxylamide* (IV).—Dry methyl alcohol (200 c.c.) containing finely powdered methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate (3 g.) in suspension was saturated at 0° with dry ammonia gas. The glucoside gradually dissolved and the solution was allowed to remain at 0° for 14 hours. After removal of the ammonia and methyl alcohol in a vacuum at 18°, the residual oil was freed from acetamide by distillation of the latter at 100°/1—2 mm. The straw-coloured syrup which remained was dissolved in water, and the solution on evaporation in a vacuum desiccator deposited the *amide* as a white solid. This crystallised from water in colourless, rectangular plates, which decomposed at 254—256° to a black mass after darkening at 245° (Found: C, 50·7; H, 5·6; N, 7·5. $C_{15}H_{18}O_7N_2$ requires C, 50·8; H, 5·6; N, 7·8%). Yield, 0·3 g. The amide is fairly soluble in alcohol and in hot water.

The filtrate after the separation of the amide was evaporated to small bulk, and a straw-coloured syrup obtained which could not be induced to crystallise. This undoubtedly consisted of impure *methyl* 3-β-*glucosidoxyindole-2-carboxylate* (III). When this syrup was heated to boiling with 6% hydrochloric acid for 1 minute, methyl 3-hydroxyindole-2-carboxylate (I) crystallised, m. p. 157—158° after recrystallisation from 70% methyl alcohol. The acetyl derivative, m. p. 145°, was identical with that described above. The syrup (1 part) was acetylated by heating it under reflux for 1 hour with fused sodium acetate (1 part) and acetic anhydride (10 parts). Water was added to the cooled mixture to decompose the excess of acetic anhydride, and methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate separated, m. p. 229—230° after recrystallisation from methyl alcohol. A mixture of the latter with an authentic specimen of the acetylated glucoside showed no depression of the melting point.

3-β-*Glucosidoxyindole-2-carboxylic Acid* (V).—A solution of potassium hydroxide (4 g.) in 80% methyl alcohol (25 c.c.) was gradually added to a suspension of methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate in methyl alcohol (50 c.c.). After the solid had dissolved, the solution was kept at room temperature for 12 hours, methyl alcohol (20 c.c.) was then added, and the mixture heated under reflux on the water-bath for 2 hours, during which time the potassium salt of 3-β-glucosidoxyindole-2-carboxylic acid crystallised

out. When cold, the colourless potassium salt was collected, washed with dry methyl alcohol, and dried. The salt (yield, 3·5 g.) was sufficiently pure for use in the next stage of the synthesis.

A solution of the potassium salt (1 g.) in water (4 c.c.) was acidified with a slight excess of 2% hydrochloric acid. The pale blue, crystalline precipitate of the *glucoside* which separated was collected and recrystallised from warm water (charcoal), from which it separated in almost colourless, rod-like prisms, which turned brown at 215—220° and decomposed to a dark liquid at 230—231° (Found: C, 53·1; H, 5·1; N, 4·0. $C_{15}H_{17}O_8N$ requires C, 53·1; H, 5·0; N, 4·1%).

A solution of this glucoside in dilute hydrochloric acid, containing ferric chloride, on boiling is quickly decomposed with the formation of indigotin. An aqueous solution when heated to boiling quickly assumes a blue colour, due to slight hydrolysis and the formation of a trace of indigotin.

1-*Acetyl*-3-*tetra-acetyl*-β-*glucosidoxyindole* (*Penta-acetylindican*) (VI).—(*A.*) Potassium 3-β-glucosidoxyindole-2-carboxylate (3·5 g.), fused sodium acetate (3·5 g.), and acetic anhydride (45 c.c.) were heated on the steam-bath for 2 hours, and then at 160—162° for 1 hour. Water (200 c.c.) was added to the cooled mixture; the penta-acetylindican then separated as an oil which gradually solidified. The solid was repeatedly crystallised from methyl alcohol (charcoal) to free it from coloured impurities, and finally from ethyl alcohol, from which it separated in glistening, colourless, elongated, rectangular prisms, m. p. 148° (yield, 4·0 g.) (Found: C, 57·2; H, 5·4. $C_{24}H_{27}O_{11}N$ requires C, 57·0; H, 5·3%). Penta-acetylindican is slightly soluble in cold and easily soluble in hot alcohol, and readily soluble in cold chloroform.

(*B.*) A suspension of methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate (6 g.) in 5% baryta water (200 c.c.), maintained at 40—45°, was vigorously agitated for 24 hours; the solid gradually dissolved. The excess of barium hydroxide was precipitated by carbon dioxide, the barium carbonate removed, and the filtrate evaporated to dryness. The residue was acetylated and *penta-acetylindican* isolated, m. p. 148°, as described above. Yield, 0·8 g.

(*C.*) A solution of potassium hydroxide (0·84 g.) in water (10 c.c.) was gradually added to one of 1-acetyl-3-hydroxyindole (VI) (*loc. cit.*) (2·1 g.) and tetra-acetyl-α-glucosidyl bromide (6·2 g.) in 100 c.c. of acetone maintained below 5° in an atmosphere of nitrogen. The mixture was kept in the ice-chest for 5 hours and then acidified with dilute acetic acid, and the acetone was removed in a vacuum at room temperature. The dark brown residual oil was dissolved in warm methyl alcohol (20 c.c.), and the solution

poured into cold water (300 c.c.); impure penta-acetylindican was then precipitated in a semi-solid condition. The glucoside crystallised from ethyl alcohol (charcoal) in glistening, colourless, elongated, rectangular prisms, m. p. 148° (yield, 0·7 g.) (Found: C, 56·8; H, 5·3; N, 2·8. $C_{24}H_{27}O_{11}N$ requires C, 57·0; H, 5·3; N, 2·6%). A mixture of the penta-acetylindican prepared in this way with that described above showed no depression of the melting point.

3-β-*Glucosidoxyindole* (*Indican*) (VIII).—1-Acetyl-3-tetra-acetyl-β-glucosidoxyindole (8 g.) quickly dissolved in absolute methyl alcohol (300 c.c.) saturated at room temperature with dry ammonia. After 24 hours, the solution was cooled to 0°, saturated with ammonia, and kept for 12 hours. The ammonia and methyl alcohol were then removed under diminished pressure at 20—25°, and the residual syrup was freed from acetamide by exposure to a high vacuum (1—2 mm.) for 1 hour at 100°. A solution of the green residue in warm water (30 c.c.) was filtered after treatment with charcoal, and exposed to a vacuum over soda-lime and calcium chloride. An almost colourless mass of crystalline indican gradually filled the liquid. Yield, 4·2 g.

The glucoside, after being twice recrystallised from water, was obtained as a mass of colourless, silky needles, m. p. 57—58°. When dried in a vacuum over sulphuric acid for 48 hours, indican lost part of its water of crystallisation; it then melted at 100—101°, became crystalline at 160°, and finally melted at 176—178°. It was obtained anhydrous, m. p. 176—178°, by heating it in the steam-oven for 3 hours, at 110° for 1 hour, and finally at 160° for 5 minutes (Found in a specimen crystallised from water and air-dried: C, 48·2; H, 6·5; N, 4·4; H_2O, 15·8. Calc. for $C_{14}H_{17}O_6N,3H_2O$: C, 48·1; H, 6·6; N, 4·0; H_2O, 15·5%. Found in an anhydrous specimen: C, 56·6; H, 6·0; N, 5·0. Calc. for $C_{14}H_{17}O_6N$: C, 56·9; H, 5·8; N, 4·8%). Anhydrous indican was also obtained from the hydrated variety in colourless prisms, m. p. 176—178°, by crystallisation from warm absolute ethyl alcohol–benzene as described by Perkin and Bloxam (*loc. cit.*).

Synthetic indican is rapidly hydrolysed in warm 3% hydrochloric acid with the liberation of glucose and indoxyl, which in the presence of acid forms "indoxyl brown." If, however, a little ferric chloride is added as an oxygen carrier and air is bubbled through the solution, the liberated indoxyl is instantaneously oxidised to almost pure indigotin. When a drop of concentrated hydrochloric acid is added to a solution of the glucoside in warm glacial acetic acid containing a little *p*-nitrosodimethylaniline as an oxidising agent, glistening leaflets of indigotin, which have a bronze reflex, quickly separate. Hydrolysis of the glucoside in warm 3%

hydrochloric acid in the presence of isatin gives a quantitative yield of indirubin, which separates in microscopic red prisms, whilst, with *p*-nitrobenzaldehyde, the liberated indoxyl forms *p*-nitrobenzaldehydeindogenide, which crystallises from acetone in red, prismatic needles, m. p. 273—274°.

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CCLII.—*Reactions of Displacement in the Tropic Acid Group. Part II.*

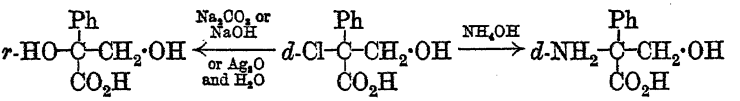
BY CARL ALOYSIUS KERR.

IN Part I, the action of sodium carbonate and of concentrated aqueous ammonia on *l*-β-chlorohydratropic acid, $CH_2Cl{\cdot}CHPh{\cdot}CO_2H$, was examined by McKenzie and Strathern (J., 1925, **127**, 82), and it now seemed of interest to prepare the optically active chlorotropic acid, $OH{\cdot}CH_2{\cdot}CPhCl{\cdot}CO_2H$, and to effect the displacement of the chlorine atom in this acid by other groups. The actions of alkali, moist silver oxide, ammonia, and reducing agents on both the active and the inactive acid were marked out for study. Moreover, the displacement of chlorine by hydrogen obviously called for inquiry, since such a change has been investigated only rarely in connexion with the Walden inversion, for example, in the reduction of *l*-chloromalic acid to *d*-malic acid (Kuhn and Zell, *Ber.*, 1926, **59**, 2514).

The preparation of *r*-chlorotropic acid is described by Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 373), who acted on atropic acid with a dilute solution of hypochlorous acid, prepared by passing chlorine into a suspension in water of freshly precipitated, yellow mercuric oxide. The author has found that this acid can be more conveniently prepared by the action of monochlorourea on atropic acid, according to the equation $CH_2{:}CPh{\cdot}CO_2H + NH_2{\cdot}CO{\cdot}NHCl + H_2O = OH{\cdot}CH_2{\cdot}CPhCl{\cdot}CO_2H + CO(NH_2)_2$. Monochlorourea has been successfully used by Detœuf (*Bull. Soc. chim.*, 1922, **102**, 176) in the preparation of the chlorohydrins of unsaturated substances, and was found in the present case to give nearly 80% yields of chlorotropic acid. The resolution of chlorotropic acid into its active components can be accomplished by means of morphine, with methyl alcohol as solvent. *d*-Chlorotropic acid has $[\alpha]_D^{18°} = +12{\cdot}6°$ for $c = 3{\cdot}025$ in methyl alcohol, and melts at

123—124°, whereas the *r*-acid has m. p. 129—130°. The rotations of chlorotropic acid in acetone and in water were considerably lower than in methyl alcohol. The first mother-liquor in the resolution contained an excess of the morphine salt of *l*-chlorotropic acid, and by five recrystallisations of this salt from methyl alcohol a morphine salt resulted which gave *l*-chlorotropic acid with $[\alpha]_D^{15°} = -12{\cdot}4°$ in methyl alcohol ($c = 3{\cdot}586$).

The action of sodium carbonate or caustic soda on *r*-chlorotropic acid gave as a main product atroglyceric acid, $OH{\cdot}CH_2{\cdot}CPh(OH){\cdot}CO_2H$, m. p. 144—145°, as well as a small quantity of a neutral oil which corresponded with the formula $C_8H_8O_2$ but could not be identified with the amount in hand. Aqueous ammonia with chlorotropic acid gave, as was expected, a chlorine-free nitrogenous substance, proved to be α-amino-β-hydroxy-α-phenylpropionic acid. *d*-Chlorotropic acid (1 mol.) when treated with moist silver oxide (2 mols.) gave *r*-atroglyceric acid, with only slight formation of the yellow neutral oil noticed in the case of alkali. The following changes can be brought about:



The action of sodium carbonate solution and of moist silver oxide on *d*-chlorotropic acid led to the formation, in both cases, of optically inactive atroglyceric acid. Such complete racemisation was not to be expected, especially in the case of silver oxide, but a similar case of complete racemisation is to be found in the action of water on *l*-α-chloro-α-phenylpropionic acid and of nitrous acid on *l*-α-amino-α-phenylpropionic acid (McKenzie and Clough, J., 1910, **97**, 1016; 1912, **101**, 390), which compounds are closely allied in structure to chlorotropic acid.

The action of concentrated ammonia on *d*-chlorotropic acid gave, on the other hand, a dextrorotatory α-amino-β-hydroxy-α-phenylpropionic acid with $[\alpha]_D^{16°} = +40{\cdot}6°$ ($c = 6{\cdot}208$) in hydrochloric acid solution. The optical purity of the amino-acid was considered to be high, but the complete proof that the optically pure acid was actually isolated was lacking owing to the difficulty of finding a suitable solvent for it. In the displacement of chlorine by the amino-group, no such extensive racemisation took place as in the formation of *r*-atroglyceric acid from *d*-chlorotropic acid. Explanation of the latter racemisation cannot be traced to the rotatory power of atroglyceric acid being low, as this acid is at present being resolved and is known to have a fairly high specific rotation.

The conversion of *r*-chlorotropic acid into tropic acid by means

of reducing agents was not accomplished, and this is in agreement with the work of McKenzie and Wood (J., 1919, **115**, 828), who found that this conversion could not be effected in the manner described by Ladenburg and Rügheimer (*loc. cit*).

EXPERIMENTAL.

Chlorotropic Acid.—Atropic acid, prepared from tropic acid by Raper's method (J., 1923, **123**, 2558), had m. p. 107—108° when recrystallised from methyl alcohol. Monochlorourea was prepared by Detœuf's method (*loc. cit.*) and its strength estimated by titration with potassium iodide and thiosulphate. Atropic acid (27 g.; 1 mol.) was mixed with 135 c.c. of water, containing 2 c.c. of glacial acetic acid, and monochlorourea solution (1½ mols.) was added. With continuous stirring for 24 hours, most of the atropic acid went into solution, the remainder going pasty. The pasty atropic acid was filtered off, washed free from chlorotropic acid with water, and recrystallised from rectified spirit; 8 g. of atropic acid were recovered. The filtrate and washings were acidified with dilute sulphuric acid and sulphurous acid was added until no reaction with starch–iodide paper was shown. The excess of sulphur dioxide was removed by boiling and the solution extracted seven times with ether. Yield, 18 g. of crude chlorotropic acid. In previous work (Ladenburg and Rügheimer, *loc. cit.*; McKenzie and Wood, *loc. cit.*), chlorotropic acid was purified by washing with cold benzene, but it was found better to recrystallise it from chloroform. Yield, 16 g. of chlorotropic acid, m. p. 129—130°.

Attempted Conversion of Chlorotropic Acid into Tropic Acid.—Ladenburg and Rügheimer (*loc. cit.*) record the reduction of chlorotropic acid with zinc and iron filings in concentrated alkali, but McKenzie and Wood (*loc. cit.*) failed to effect the reduction either by this means or by means of sodium amalgam, zinc and hydrochloric acid, or caustic soda and aluminium. 3 G. of chlorotropic acid, made into a paste with 20 g. of moist copper–zinc couple, were treated with concentrated hydrochloric acid and the mixture was heated on a water-bath for 4 hours. The sludge was separated by decanting off the liquid, and then washed with hot water. Four ether extractions of the acid liquor and washings gave a yellow oil which crystallised on standing. After two recrystallisations from hot chloroform, the crystals melted at 117—122°, but a mixture with pure tropic acid (m. p. 117—118°) had a m. p. 90—93°. After heating 3 g. of chlorotropic acid, 10 g. of copper–zinc, and 100 c.c. of hydrochloric acid (4*N*) for 23 hours, and isolating the product as before, 2 g. of white solid, containing chlorine, and of m. p. 114—116°, were isolated from the ethereal extracts. A fractional

crystallisation of this substance from water gave 0·7 g. of chlorotropic acid (m. p. 128—130°). 3 G. of chlorotropic acid, 50 c.c. of water, and an excess of zinc foil were kept in a platinum basin for two months and then treated with an excess of dilute sulphuric acid. The yellow oil obtained by extraction with ether crystallised to give a solid, m. p. 105—117°, which contained chlorine.

Action of Sodium Hydroxide on r-*Chlorotropic Acid.*—3 G. of chlorotropic acid were neutralised with 155 c.c. of caustic soda (*N*/10), and 154 c.c. of caustic soda further added with a drop of phenolphthalein. After 1 hour's heating on the water-bath the colour of the indicator faded. The cooled mixture was made alkaline, and the neutral oil removed by extraction with ether four times. Yield, 0·5 g. The alkaline solution was made acid with dilute sulphuric acid and extracted five times with ether. From the dried ethereal extracts, 1·1 g. of crystalline acid were obtained, which furnished 0·7 g. of an acid, m. p. 141—145°, when recrystallised from hot ethyl acetate. A second recrystallisation from the same solvent gave 0·5 g. of atroglyceric acid, m. p. 145—147°, (Fittig and Kast, *Annalen*, 1881, **206**, 32, give m. p. 146°) (Found: C, 59·3; H, 5·6. Calc., C, 59·3; H, 5·5%).

Action of Sodium Carbonate on r-*Chlorotropic Acid.*—2 G. of chlorotropic acid were neutralised with approximately *N*-sodium carbonate (9 c.c.), a drop of phenolphthalein was added, and a further 8·5 c.c. of sodium carbonate were run in. After 10 minutes on the water-bath, the colour of the indicator was discharged, and boiling was continued for 20 minutes. The cooled mixture, made alkaline, was extracted with ether to remove a small quantity of neutral oil. Five ether extractions of the acidified liquor gave 1 g. of solid, m. p. 130—138°, which, after recrystallisation from water, had m. p. 144—145°. It was chlorine-free and identified as atroglyceric acid.

α-*Amino*-β-*hydroxy*-α-*phenylpropionic Acid.*—A solution of 3 g. of chlorotropic acid in 50 c.c. of concentrated ammonia, saturated at 0°, was kept in a stoppered bottle for 7 days at the ordinary temperature, and then transferred to a crystallising dish. After 16 hours' standing, 2·2 g. of an acid, washed free from ammonium chloride by water, were separated. The acid was chlorine-free, gave no ammonia with caustic alkali, and behaved as an amino-acid, being soluble in acid and in alkali. It was purified by dissolving it in caustic soda and making the solution exactly neutral with hydrochloric acid. A yield of 1·3 g. of pure acid was obtained from 1·4 g. of crude acid. α-*Amino*-β-*hydroxy*-α-*phenylpropionic acid* has m. p. 285—288° (decomp.) and is insoluble in the commoner organic solvents and in water (Found: C, 59·8; H, 6·0. $C_9H_{11}O_3N$

requires C, 59·7; H, 6·1%). Its *hydrochloride* separates in rhombic prisms, m. p. 225° (decomp.).

Preparation of Optically Active Chlorotropic Acid.—A solution of 30 g. of chlorotropic acid in 300 c.c. of hot methyl alcohol was added to a solution of 45 g. of morphine in 3400 c.c. of methyl alcohol, and the mixture heated just to boiling. On cooling, crystallisation began, and after 18 hours the resulting 45 g. of very fine needles were dissolved by heating in 3750 c.c. of methyl alcohol. On concentration to 1850 c.c., the solution, after 48 hours, gave 24 g. of crystals which were dissolved by heating with 2500 c.c. of methyl alcohol. The solution was concentrated to 1250 c.c. and after 24 hours 15 g. of morphine chlorotropate, crystallising in fine needles, were separated. The acid was obtained by acidification with dilute sulphuric acid and extraction with ether. Yield, 5·8 g. with $[\alpha]_D^{18°} = +11·2°$ ($c = 3·5565$) in methyl alcohol. Three successive crystallisations of this dextro-acid from chloroform gave acids with the following rotations in methyl alcohol: $[\alpha]_D^{17°} = +12·0°$ ($c = 3·052$), $[\alpha]_D^{18°} = +12·5°$ ($c = 3·1245$), $[\alpha]_D^{18°} = +12·6°$ ($c = 3·025$). The pure d-*chlorotropic acid* has therefore $[\alpha]_D^{18°} = +12·6°$ ($c = 3·025$) in methyl alcohol. It melts at 123—124° (Found: C, 53·8; H, 4·5. $C_9H_9O_3Cl$ requires C, 53·8; H, 4·5%). The first mother-liquor in the resolution was evaporated to small bulk, and 29 g. of morphine salt were separated. This was recrystallised five times from methyl alcohol, and the resulting salt on decomposition gave l-*chlorotropic acid* with $[\alpha]_D^{15°} = -12·4°$ ($c = 3·586$) in methyl alcohol.

Action of Sodium Carbonate on d-*Chlorotropic Acid.*—1 G. of dextrorotatory chlorotropic acid, with $[\alpha]_D^{16°} = +10·3°$ in methyl alcohol, was neutralised with 7·4 c.c. of sodium carbonate (0·5745*N*) and 7·2 c.c. of the alkali were further added, with a drop of phenolphthalein. After heating for 10 minutes on the water-bath, the solution became colourless; it was made alkaline, and the neutral oil removed by extraction with ether. The solution was acidified with dilute sulphuric acid, and the acid extracted with ether. 0·3 G. of chlorine-free solid was obtained. This was atroglyceric acid and it was quite inactive ($c = 2·618$) in methyl alcohol.

Action of Silver Oxide on d-*Chlorotropic Acid.*—1 G. (1 mol.) of dextrorotatory chlorotropic acid with $[\alpha]_D^{16°} = +10·3$ in methyl alcohol, and the silver oxide obtained from 1·7 g. (2 mols.) of silver nitrate by precipitation with caustic soda, were mixed with 50 c.c. of water and stirred mechanically for 2 hours. After 60 hours at the ordinary temperature, the mixture was heated for ½ hour, and the silver chloride removed by precipitation with hydrochloric acid. By extraction of the filtrate with ether 0·2 g. of solid, m. p. 143—

146°, was obtained. A mixture of this with atroglyceric acid had m. p. 143—145°, and therefore the substance was atroglyceric acid. It was completely inactive ($c = 1{\cdot}764$) in methyl alcohol.

Action of Aqueous Ammonia on d-*Chlorotropic Acid.*—A solution of 1 g. of *d*-chlorotropic acid with $[\alpha]_D^{18^\circ} = +12{\cdot}6^\circ$ in methyl alcohol, in 10 c.c. of concentrated ammonia, saturated at 0°, was kept in a stoppered bottle for 10 days and then transferred to a crystallising dish. After 3 days, all the solvent had evaporated and the remaining solid was washed free from ammonium chloride and dried. Yield, 0·6 g. of α-amino-β-hydroxy-α-phenylpropionic acid. The rotation of the amino-acid was $[\alpha]_D^{16^\circ} = +40{\cdot}6^\circ$ in *N*-hydrochloric acid ($c = 6{\cdot}208$). Failure attended the attempts to raise the rotation of this acid, either by repeated precipitation from its solution in caustic soda by means of hydrochloric acid, or by recrystallisation from concentrated aqueous ammonia. A saturated solution of ammonia in *sec.*-octyl alcohol does not convert chlorotropic acid into the corresponding amino-acid.

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UNIVERSITY COLLEGE, DUNDEE,
UNIVERSITY OF ST. ANDREWS. [*Received, June 17th,* 1927.]

CCLIII.—*Methylmercuric Halides and Hydroxide.*

By LEONARD ERIC HINKEL and THOMAS HUBER ANGEL.

AN attempt to repeat Marvel and Gould's preparation of methylmercuric iodide by the action of magnesium methyl iodide upon an excess of mercuric chloride suspended in ether (*J. Amer. Chem. Soc.*, 1922, **44**, 153) resulted only in the production of the double compound $CH_3{\cdot}HgCl,2CH_3{\cdot}HgI$ and a small quantity of methylmercuric chloride. If the Grignard reagent was added very slowly to the suspension of mercuric chloride, a copious precipitate of mercuric iodide soon formed, which readily dissolved on further addition of the reagent. The formation of mercuric iodide can be explained by assuming that the methylmercuric iodide produced by reaction (1) reacts with the excess of mercuric chloride in accordance with equation (2).

$$CH_3{\cdot}MgI + HgCl_2 = CH_3{\cdot}HgI + MgCl_2 \quad . \quad . \quad . \quad (1)$$

$$2CH_3{\cdot}HgI + HgCl_2 = 2CH_3{\cdot}HgCl + HgI_2. \quad . \quad . \quad (2)$$

In support of this assumption, it was found that the latter reaction occurs readily in alcoholic or ethereal solution. The subsequent

solution of mercuric iodide on further addition of the Grignard reagent is explained by their interaction as represented by the equation (3).

$$CH_3{\cdot}MgI + HgI_2 = CH_3{\cdot}HgI + MgI_2 \quad . \quad . \quad . \quad (3)$$

This reaction proceeds smoothly and serves as a convenient method for the preparation of methylmercuric iodide in quantity. The fact that the double compound $CH_3{\cdot}HgCl,2CH_3{\cdot}HgI$ was obtained instead of methylmercuric iodide in the repetition of Marvel and Gould's experiment adds further support to the above assumption, since it was observed that from a hot alcoholic solution of methylmercuric chloride and iodide the stable double compound crystallised on cooling. The double compound is converted by mercuric chloride into methylmercuric chloride, and it is probable that the small amount of the latter which was found associated with the double compound in the original reaction product owed its origin to this cause, since the amount formed increased with the excess of mercuric chloride originally employed. From a consideration of these facts, it would appear impossible to obtain methylmercuric iodide under the conditions of Marvel and Gould.

Methylmercuric hydroxide has long been known in solution (Frankland, *Annalen*, 1853, **85**, 368; Dunhaupt, *ibid.*, 1854, **92**, 381; *J. pr. Chem.*, 1854, **61**, 399; Crymble, J., 1914, **105**, 666), but it was first isolated in the solid form by Sneed and Maynard (*J. Amer. Chem. Soc.*, 1922, **44**, 2946) from methylmercuric iodide and moist silver oxide in the presence of a small amount of alcohol.

Sneed and Maynard's method of purification of the base—precipitation from saturated alcoholic solution with a large excess of dry ether—is very wasteful, for large quantities of ether are necessary, the base undergoes much decomposition in its presence, and five repetitions of the process do not effect complete purification (m. p. 104°). A method is now described whereby the purification can be efficiently and rapidly achieved without loss of material. The pure base so obtained differs from that prepared by Sneed and Maynard both in melting point and in solubility.

Experimental.

Action of Magnesium Methyl Iodide on Mercuric Chloride.—The Grignard reagent prepared from 2·4 g. of magnesium was added to 30 g. of finely powdered mercuric chloride suspended in 250 c.c. of dry ether under the conditions described by Marvel and Gould (*loc. cit.*). The crude product was crystallised from hot thiophen-free benzene and then fractionally from methyl alcohol, the less soluble mercuric iodide and methylmercuric chloride being thereby removed; the final product was obtained in small, pearly leaflets, m. p. 129°

(Found: Cl, 4·0; I, 27·1. $C_3H_9ClI_2Hg_3$ requires Cl, 3·8; I, 27·0%). The double compound differs from methylmercuric chloride in having a much more intense and unpleasant odour.

Methylmercuric iodide was prepared under the conditions previously described, mercuric chloride being replaced by the equivalent amount of mercuric iodide. The product crystallised from methyl alcohol in transparent, rectangular plates melting at 145° and not 143° as stated in the literature (Found: I, 36·9. Calc.: I, 37·05%).

Methylmercuric Hydroxide.—Methylmercuric iodide (10 g.) in 50 c.c. of methyl alcohol and 2 c.c. of water was mechanically agitated for 3 hours with 7 g. of moist silver oxide containing 34% of water. The filtered solution was evaporated to dryness in a vacuum at 40°, the white residue warmed to 30° with 20 c.c. of chlorobenzene, in which it was very sparingly soluble, and alcohol added until solution was just effected, the temperature being kept at 30°; the alcohol was then removed in a vacuum over sulphuric acid, and the base, which separated in small crystals, was drained from the chlorobenzene and washed with light petroleum (previously treated with alcoholic potassium hydroxide to remove sulphur compounds, since these react readily with methylmercuric hydroxide). This process of purification was repeated several times; the base then obtained, after drying in a vacuum, melted at 106° (Found, by Rupp and Nöll's method, Meyer's "Lehrbuch der Organisch-Chemischen Methodik," 1922, p. 359: Hg, 86·0. Calc. for CH_4OHg: Hg, 86·2%). The pure base forms white crystals with a pearly lustre having a faint, unpleasant odour. It decomposes slowly on standing, more rapidly in presence of ether. When heated above its melting point, it partly decomposes and then detonates violently. Contrary to the statements of Sneed and Maynard, it is very sparingly soluble in cold benzene, toluene, carbon tetrachloride, and light petroleum.

The authors desire to thank Professor J. E. Coates for his constant help and interest in this investigation.

UNIVERSITY COLLEGE, SWANSEA. [*Received, June 1st*, 1927.]

CCLIV.—*The Alkaloids of* Picralima Klaineana.

By THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP.

IN December, 1923, we received from the Imperial Institute a supply of "Akuamma" seeds which had been forwarded by the Department of Agriculture in the Gold Coast Colony, accompanied by herbarium specimens of the plant, which had been identified

by the Director of the Royal Botanic Gardens, Kew, as those of *Picralima Klaineana*, Pierre. A full account of the botany of the plant and of the use of the seeds as a febrifuge in native medicine has been published by Holmes (*Pharm. J.*, 1915, **41**, 758; 1922, **55**, 478). Last year Frère Just Gillet, Curator of the Botanical Gardens at Kisantu, Belgian Congo, sent us a small supply (300 g.) of seeds which also were identified at Kew as derived from a species of Picralima, probably *P. Klaineana*. In spite of its reputation as the source of a useful drug, at least among African natives, *P. Klaineana* does not seem to be widely distributed and Frère Gillet reports that he had to make a tedious journey of some 30 leagues to collect his small sample. We are therefore the more indebted to the authorities of the Imperial Institute and in particular to the officers of the Department of Agriculture in the Gold Coast Colony, for the supplies of seed we have examined.

Beyond the preliminary work referred to in the articles by Holmes (*loc. cit.*), there appeared, when we began this work, to be no record of the chemical examination of any species of *Picralima*, but two papers have been published recently by Clinquart (*Bull. Acad. Roy. Med. Belge*, 1926, 492; *J. Pharm. Belg.*, 1927, **9**, 187) giving results of a preliminary examination of the seeds, bark and leaves also supplied by Frère Gillet. Clinquart obtained a few centigrams of a crystalline alkaloid, m. p. 242—243°, and a large amount of an amorphous alkaloid. The behaviour of these two alkaloids with the usual precipitants and colour-producing reagents is described, but no attempt is made to characterise either alkaloid or its salts in detail. In view of the publication of these two papers it has been considered desirable to place on record the data now presented. The seeds of *P. Klaineana* contain at least four alkaloids, two of which have been crystallised. Only one of these has so far been obtained in sufficient quantity for characterisation and this, which is no doubt identical with Clinquart's crystalline base, it is proposed to call *akuammine* from "akuamma," one of the native names of *P. Klaineana* in the Gold Coast. Akuammine has the formula $C_{22}H_{28}O_4N_2$, yields a series of well-crystallised salts, gives a number of characteristic colour reactions with aromatic aldehydes in presence of hydrochloric acid, and contains one methoxyl, one hydroxyl, and one methylimino-group. The last probably represents a tertiary nitrogen atom, since akuammine furnishes a well-crystallised *monomethiodide*, which decomposes on heating, evolving a fishy odour, doubtless due to dimethylamine. The alkaloid does not react with semicarbazide or other reagents for carbonyl groups and no evidence of a methylenedioxy-group is afforded with Gaebel's reagent. The state of the remaining nitrogen has not been ascer-

tained; on treatment in hydrochloric acid solution with sodium nitrite, a scarlet hydrochloride is formed, which does not give Liebermann's nitrosoamine reaction and appears to be a nitro-derivative of akuammine. Akuammine is converted by alkalis under certain conditions into a *monohydrate*, which crystallises with some difficulty. The latter is also formed on hydrolysis of acetylakuammine by alkali, and an O-*methyl* derivative of the monohydrate appears to be produced when akuammine is treated with methyl iodide in presence of alkali. One or both of the remaining oxygen atoms are no doubt involved in these changes.

The other three alkaloids, referred to subsequently as A, B, and D, we propose to examine fully as soon as material is available. Names are not suggested for them, as they may prove to be related to akuammine, in which case it may not be necessary to add to the already large trivial nomenclature of alkaloids. Alkaloid D is remarkable in having a specific rotation of $-737°$ in alcohol or chloroform. Neither A nor B has yet been obtained crystalline.

Both the Congo and the Gold Coast seeds yield akuammine and alkaloids A and B, but only one sample of Gold Coast seeds has so far yielded alkaloid D.

EXPERIMENTAL.

The finely ground seeds were extracted in a copper Soxhlet apparatus first with petroleum, b. p. 60—80°, to remove fat and then with 96% alcohol. The alcoholic extract was taken to dryness under reduced pressure, and the residue treated with successive quantities of 2% hydrochloric acid until alkaloid was no longer removed. The mixed acid liquors were shaken out with ether to remove resinous and waxy impurities and then diluted with water until no further precipitation took place. The precipitate at this stage consists of a weakly basic alkaloid or mixture of alkaloids (A), from which no crystalline material has so far been obtained. The filtrate from this was digested with charcoal for 1 hour on a water-bath, filtered, allowed to cool, and then treated with saturated sodium carbonate solution in excess; this precipitated a mixture of alkaloids as a brown powder, which was collected, washed with hot water, and dried in a vacuous desiccator. The dry mixture was then extracted with ether in a Soxhlet apparatus and so separated into a further quantity of material apparently identical with (A), which remained undissolved in the extractor, and a partly crystalline powder, which gradually accumulated in the extraction flask. When the ether ceased to extract alkaloid, the solvent was distilled off and the dry residue macerated with twice its weight of alcohol, which dissolved a second amorphous alkaloid (B), and left a partly

crystalline residue of crude akuammine (alkaloid C). The latter was collected, washed with a little alcohol, allowed to dry in the air, and then treated with a slight excess of *N*-sulphuric acid (2·8 c.c. approx. per gram) and sufficient water to dissolve it on boiling. The hot solution was treated with charcoal and filtered. On cooling, thin, colourless needles (m. p. 214—218°) of crude akuammine sulphate separated. The mother-liquor on concentration in a vacuous desiccator deposited more of the same sulphate, but finally dried up to a brown varnish. From this, by solution in dry alcohol, a further crop of akuammine sulphate can be obtained, but eventually an amorphous residue of the sulphate of alkaloid B is left. If ammonia solution is used in place of sodium carbonate for precipitation, the residue left after the removal of most of the akuammine sulphate sets to a jelly due to the presence of the sulphate of a hydrate of akuammine formed by the action of ammonia on this alkaloid as described later (p. 1958).

The cold alcoholic extract of the ether-soluble portion of the precipitated alkaloids was taken to dryness under reduced pressure, dissolved in sufficient *N*-sulphuric acid to form a faintly acid solution, and to this was added a saturated aqueous solution of sodium iodide in water until no further precipitation occurred. After standing for a week, the clear liquor was poured off and the mixture of tar and crystalline matter that had separated was triturated with a little cold absolute alcohol, which dissolved the tar and left a small quantity of akuammine hydriodide. The alcoholic washings were added to the mother-liquors, and the whole was fractionally precipitated with sodium carbonate solution, the first few drops of precipitant serving to remove a dark brown, sticky base, from which a clear pale yellow mother-liquor was poured off. This on further addition of sodium carbonate solution yielded the crude alkaloid (B) as a pale yellow powder, m. p. 104° (air-dry) or 167° (dried in a vacuum).

The seeds received from the Imperial Institute consisted of several samples collected at different times, and from one of these, on recrystallisation of the crude akuammine sulphate as described above, the first fraction consisted of the well-crystallised sulphate of alkaloid (D) (p. 1958). As only 2 g. of this alkaloid have been obtained, it has been considered advisable to conserve it for the present and only to make such observations upon it as would not entail the loss of material. It is therefore only possible to put its chief characteristics on record.

The quantity of alkaloids present in *P. Klaineana* seeds is more than 5%, but the exact amount cannot be determined by any of the ordinary methods of estimation, because the alkaloids cannot

be precipitated completely from solution in acids by alkalis, nor can the alkaloid left in such alkaline filtrate be completely removed by any of the ordinary immiscible solvents. The yield of crude akuammine is about 0·6%. The four alkaloids are readily differentiated by their physical properties and colour reactions. Alkaloid A is insoluble in all ordinary solvents except acids and alkalis, and from these it is precipitated on dilution with water. Alkaloid B is readily soluble in all ordinary solvents except water, and solutions of its salts, unlike those of any of the other three, give an intense indigo-blue colour with ferric chloride. Akuammine (alkaloid C) dissolves in concentrated sulphuric acid without coloration, but gives an intense blood-red colour, stable for several days, with nitric acid. The second crystalline alkaloid (D) gives no colour with sulphuric acid but a vivid green, fading to yellow in a few hours, with nitric acid.

In the following descriptions, the " melting points " are corrected; in each case, except for akuammine hydrate, they are points at which the substance froths up the tube. The temperature at which this occurs varies with the rate of heating, *e.g.*, pure akuammine hydrochloride can be made to melt and decompose at any temperature from 215° to 227°. The melting points recorded for the base and its salts were taken alongside the pure hydrochloride, melting at 227°, so that they are comparable among themselves. The optical rotations are for the dried substance in each case.

Akuammine (Alkaloid C).

The base is prepared by adding excess of sodium carbonate solution to a warm, aqueous solution of a purified salt. It is sparingly soluble in cold alcohol, but once dissolved in boiling alcohol it crystallises from the latter only by spontaneous evaporation in minute, colourless needles, m. p. 255°, $[\alpha]_D^{20°}$ −66·7° (in alcohol; c = 0·504) or −73·4° (in chloroform; c = 0·8716). It is rather more soluble in chloroform and sparingly soluble in acetone or ether (Found: C, 69·0, 69·1; H, 7·2, 7·0; N, 7·5. $C_{22}H_{28}O_4N_2$ requires C, 68·7; H, 7·3; N, 7·3%).

Akuammine hydrobromide, prepared like the sulphate (see above), separates from dilute hot aqueous or alcoholic solutions in faintly grey, long, slender prisms, or from concentrated solutions in the same solvents in small needles, m. p. 228°, $[\alpha]_D^{20°}$ −26·05° (in water; c = 0·6076). The air-dry salt loses in a vacuous desiccator 3·61% and no further loss takes place in a vacuum at 100°. (Calc. for $C_{22}H_{28}O_4N_2,HBr,H_2O$: H_2O, 3·7%. Found for dry salt: C, 56·1, 56·3; H, 6·0, 6·1; Br, 16·6. $C_{22}H_{28}O_4N_2,HBr$ requires C, 56·7; H, 6·3; Br, 17·1%). The *hydrochloride* closely resembles the

hydrobromide in appearance, but is of paler colour and rather more soluble in water or alcohol. It has m. p. 227° and $[\alpha]_D^{20°}$ −26·6° (in water; $c = 0{\cdot}8769$) or −32·8° (in alcohol; $c = 1{\cdot}716$) and crystallises with one molecule of water (Found: loss in a vacuum at 120°, 4·0. $C_{22}H_{28}O_4N_2,HCl,H_2O$ requires H_2O, 4·1%. Found for dry salt: C, 62·5, 62·6; H, 6·9, 6·7; N, 7·1; Cl, 8·5, 8·4. $C_{22}H_{28}O_4N_2,HCl$ requires C, 62·7; H, 7·0; N, 6·6; Cl, 8·4%). The *sulphate*, prepared as described above, crystallises from hot water or hot alcohol in rosettes of flattened needles, which rapidly become red on exposure to light. It melts at 221° and has $[\alpha]_D^{19°}$ −40·3° (in water; $c = 2{\cdot}0868$). The salt is abnormal in composition, crystallises with 10 molecules of water of crystallisation, of which 9 are lost at atmospheric temperature in a vacuous desiccator over calcium chloride. Loss (*a*) from air-dry salt at 100° in a vacuum, 11·5; (*b*) from salt previously dried to constant weight in a vacuous desiccator, 1·8. $(C_{22}H_{28}O_4N_2)_3,2H_2SO_4$, for $10H_2O$, requires H_2O 11·8%, and for $1H_2O$ 1·3% [Found for dry salt: C, 58·8; H, 6·7; S, 4·45. $(C_{22}H_{28}O_4N_2)_3,2H_2SO_4$ requires C, 58·7; H, 6·5; S, 4·7%]. This may be a double compound consisting of one molecule of the acid salt with one molecule of the normal salt (B,H_2SO_4; B_2,H_2SO_4). In this connexion, it may be noted that another dibasic acid, *viz.*, oxalic acid, yields at least three salts, which, however, have not been satisfactorily separated.

The *hydriodide* is precipitated as a crystalline powder on adding potassium iodide to even a dilute solution in water of any soluble salt of akuammine. It cannot be crystallised from hot water without decomposition, but separates from hot alcohol in anhydrous, minute, pale grey needles, m. p. 226° (Found: C, 52·0; H, 6·0. $C_{22}H_{28}O_4N_2,HI$ requires C, 51·5; H, 5·7%).

The *nitrate*, also prepared by precipitation, crystallises from boiling alcohol in pale cream-coloured needles, m. p. 224°. The *thiocyanate*, similarly prepared, crystallises from alcohol in pale greyish needles, m. p. 218°. The *perchlorate*, precipitated by addition of sodium perchlorate to a solution of the hydrochloride in water, crystallises from hot alcohol in colourless, spheroidal granules, m. p. 215°, if the solution is concentrated, and from more dilute solutions in colourless needles also melting at 215°. This salt becomes pink on exposure to air and resinous after several crystallisations from boiling alcohol. The *picrate* crystallises from hot alcohol in rosettes of brilliant yellow needles, m. p. 199°. The *picrolonate*, precipitated in minute, yellow needles, darkens at 160° and froths at 194°. On dissolution in hot alcohol it deposits a deep blue dye.

No chloroaurate has been prepared, as akuammine hydrochloride,

reduces gold chloride immediately. It also reduces platinic chloride and silver nitrate in the cold and Fehling's solution on warming.

Methoxyl and methylimino-groups. Determinations of these groups were made on the base and the hydrochloride (Found for base : MeO, 8·87 ; NMe, 8·2. Calc. for MeO, 8·0 and for NMe, 7·5%. Found for hydrochloride : MeO, 7·73 ; NMe, 6·6. Calc. for MeO, 7·4 and for NMe, 6·9%).

Akuammine hydrochloride gives (1) a rose-red colour with vanillin or piperonal in presence of hydrochloric acid, (2) a yellowish-brown colour with dimethylaminobenzaldehyde (Ehrlich's reagent), changing on long standing to red with a green fluorescence, (3) with bromine water a pink colour, the solution becoming cloudy on further addition of bromine.

Action of methyl iodide on akuammine. The pure base does not dissolve in methyl iodide, but when suspended in the reagent the latter gradually contracts in volume and in about 2 days conversion into a *monomethiodide* appears to be complete. This separates from solutions in hot methyl alcohol in rosettes of colourless prisms, m. p. 274°. On melting, the substance froths vigorously and gives off a vapour with a fishy odour, probably due to dimethylamine. The methiodide in solution gives no precipitate with alkali hydroxides or carbonates and is therefore the iodide of a quaternary base (Found: C, 52·7 ; H, 5·7 ; I, 24·4 ; MeO, 6·8 ; NMe, 9·7. $C_{22}H_{28}O_4N_2,CH_3I$ requires C, 52·4 ; H, 5·9 ; I, 24·1 ; MeO, 5·9 ; 2NMe, 11·1%). The results for methoxyl are high and those for methylimino-groups low. In carrying out these estimations, it was noticed that elimination of methyl iodide in the second stage (methylimino-determination) began at the low temperature of 180°, immediately after addition of ammonium iodide, so that it appears likely that part of the methyl iodide collected in the earlier stage (methoxyl determination) is really due to methylimino-groups. The total amount of methyl iodide formed in the estimation, calculated from the amount of silver iodide weighed, was 79·07%, whilst there should be formed, assuming the presence of one methoxyl and two methylimino-groups, 80·9%. Cases in which there is no sharp distinction between the conversion of methoxyl and methylimino-groups into methyl iodide in such estimations have been observed previously, *e.g.*, in ergotoxine (Barger and Ewins, J., 1918, **113**, 235 ; a summary of literature on this subject is given on page 237).

Action of methyl iodide and alkali on akuammine. Akuammine base (1 g.) was dissolved in *N*-sodium methoxide solution in methyl alcohol (2·7 c.c.), and methyl iodide (4 c.c.) was added. This mixture, after standing for 4 days, was boiled for 4 hours. The liquid was taken to dryness under reduced pressure, and the residue

dissolved in boiling water, from which it separated on cooling as a colourless oil. The solution in water gives a precipitate of a new oily base on addition of sodium carbonate or alkali hydroxide. Neither the base nor any of its salts, except the picrate, have so far been induced to crystallise. The *picrate* is precipitated on adding picric acid in methyl alcohol to a solution of the base or the hydriodide in the same solvent, and can be crystallised either from boiling water or from methyl alcohol, producing in the former case canary-yellow needles or rosettes of needles and in the latter bronze-tinted, dense rosettes of prisms, both forms melting at 205° (Found : MeO, 10·0; NMe, 6·0. $C_{22}H_{29}O_5N_2\cdot CH_3,C_6H_3O_7N_3$ requires 2MeO, 9·6; NMe, 4·5%). These results agree with the assumption that in this reaction the akuammine is first hydrated by the alkali (see below) and that the hydrate undergoes *O*-methylation either on the hydroxyl group originally present in akuammine or on a new group formed in the hydration.

Acetylation of akuammine. The pure base (3·8 g.) was boiled for 5 minutes with acetic anhydride (10 c.c.), the solution left to cool, and the excess of reagent removed by distillation under reduced pressure. The residue was dissolved in water, the liquid poured into sodium carbonate solution, and the precipitate collected, sucked dry on the filter, and dissolved in the minimum quantity of boiling alcohol, from which it separated on cooling in rosettes of colourless prisms (yield, 2·4 g.), m. p. 226°. The melting point was not changed by recrystallisation. The concentrated mother-liquors, which had ceased to deposit crystals, were taken to dryness, the residue was dissolved in four times its weight of boiling *N*/2-hydrobromic acid, and the solution filtered hot. On cooling, it deposited a silky mass of hair-like needles, m. p. 236°, of *acetylakuammine hydrobromide* (yield, 1·1 g.), the melting point of which remained unchanged on recrystallisation. This hydrobromide on solution in boiling water and precipitation with sodium carbonate solution furnished the pure *base*, m. p. 226°. From the mother-liquors of the hydrobromide the rest of the acetylated base was precipitated as the *picrate* (0·5 g.), which crystallised with difficulty from concentrated solutions in methyl alcohol, in gelatinous masses of rosettes of minute, yellow needles, m. p. 168° after drying in air. The acetylated base becomes pink on exposure to air and has $[\alpha]_D^{20°}$ −52·08° ($c = 0·64$ in alcohol) (Found for the base : C, 67·5, 67·45; H, 6·9, 6·7; MeO, 9·3; NMe, 6·9; acetic acid formed on alkaline hydrolysis, 13·1. $C_{22}H_{27}O_4N_2\cdot CO\cdot CH_3$ requires C, 67·6; H, 7·1; MeO, 7·3; NMe, 6·8; acetic acid, 14·1%. Found for hydrobromide : C, 57·3, 57·1; H, 5·9, 6·0; Br, 15·95. $C_{22}H_{27}O_4N_2\cdot CO\cdot CH_3,HBr$ requires C, 56·8; H, 6·2; Br, 15·75%).

The base recovered from the acetic acid estimation appeared to be akuammine hydrate, m. p. above 300° (see below).

Action of alkalis on akuammine. Akuammine dissolves slowly in solutions of ammonia or alkali hydroxides, forming in the course of a few days dark brown liquids, which on neutralisation by acids deposit precipitates of a mixture of bases. For the examination of these products it has been found most convenient to treat akuammine with a known quantity of a normal solution of sodium ethoxide in alcohol, in which it dissolves immediately, keep the solution for several days, remove the alcohol, and treat the residue with water; the sodium derivatives presumably first formed and stable in alcohol are then almost completely dissociated, leaving a dark brown precipitate. The latter on digestion first with alcohol and then with chloroform is obtained as a nearly colourless powder, which does not sinter up to 300° and after heating to this temperature can usually be shaken out of the melting point tube as an orange-brown powder. The product is insoluble in all ordinary solvents, and is finally purified by dissolving it in a known quantity of sodium ethoxide in alcohol, adding sufficient alcohol to dilute the solution to a concentration of about 1 part in 5 parts, and then neutralising the filtered liquid with the calculated quantity of *N*/2-acetic acid; after a few minutes, practically the whole of the product crystallises in small, spheroidal granules of minute needles, which do not sinter or melt up to 310°. It dissolves immediately in solutions of ammonia or alkali hydroxides, but such solutions gelatinise when carbon dioxide is passed into them: the jelly can be filtered out and dries up to a brown powder having the characters of the original substance. The product appears to be an *akuammine hydrate* formed by addition of a molecule of water to akuammine (Found: C, 65·0, 65·1; H, 6·9, 6·8. $C_{22}H_{28}O_4N_2,H_2O$ requires C, 65·6; H, 7·5%). The yield in the above process has varied from 15 to 41% of the akuammine used. The by-products soluble in alcohol and chloroform are brown, amorphous substances soluble in alkalis, but they also form salts, *e.g.*, hydrobromides, which are sparingly soluble in cold water or saline aqueous solutions but very readily soluble in alcohol, acetone, or chloroform.

Base D.

The akuamma seeds used for this work consisted of a number of samples and from one of these the crude alkaloidal sulphates, prepared as described on p. 1953, on recrystallisation from water gave a fraction crystallising in colourless, transparent, flattened cubes. This *sulphate*, m. p. 161°, $[\alpha]_D^{14°}$ −594·1° ($c = 0·4226$ in water) or −539·8° ($c = 0·2860$ in water), contains 8·9% of water

of crystallisation, of which 2·4% is lost in a vacuous desiccator at atmospheric temperature. The *base*, obtained by adding sodium carbonate solution to an aqueous solution of the sulphate, crystallises from hot alcohol in brilliant, colourless leaflets, m. p. 177·5°, $[\alpha]_D^{19°}$ −737·5° (c = 0·4932 in alcohol), −737·7° (c = 0·3504 in chloroform). The *nitrate* forms colourless needles, m. p. 180—181°. The *picrate* can be crystallised by dissolving it in boiling chloroform and adding an equal volume of boiling alcohol. From this mixture on cooling, it separates in dull yellow needles, m. p. 169°.

Base D gives a grass-green coloration when a mere trace is added to a drop of concentrated nitric acid. Like akuammine, it gives colours with aromatic aldehydes in presence of hydrochloric acid, *viz.*, indigo-blue with vanillin and magenta with piperonal, both changing to bright ultramarine-blue after a few days and remaining stable for at least 14 days. The alkaloid gives no coloration with Gaebel's test for methylenedioxy-groups.

The authors are indebted to the late Mr. S. E. Pusey and to Messrs. L. Barnett and H. C. Clarke for much assistance in the extraction of the alkaloids and in the analyses of the various preparations described.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

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CCLV.—*The Isomerism of the Oximes. Part XXXI. The Furfuraldoximes and 2-Methoxy- and 4-Methoxy-1-naphthaldoximes.*

By OSCAR LISLE BRADY and RICHARD FRANK GOLDSTEIN.

THE greater part of the study of the aldoximes from the point of view of stereoisomerism has been devoted to those in which the aldoximino-group is attached to the benzene ring. The stability of the α-isomeride in the benzaldoximes, in contrast with the aliphatic aldoximes where the β-form is the normal product, makes it of some interest to consider the effect of other ring systems on the relative stability of the two isomerides. The case of furfuraldoxime is of historic importance, since this was the first aldoxime to be obtained in two forms (Odernheimer, *Ber.*, 1883, **16**, 2988). Goldschmidt and Zanoli (*Ber.*, 1892, **25**, 2573) also prepared the two isomerides and determined their configuration, but thought they found indications of abnormal behaviour, since in the acetylation of the α-oxime and subsequent hydrolysis some furfuronitrile and a mixture of the two oximes were obtained. Similarly, Minunni

(*Gazzetta*, 1896, **26**, i, 463) obtained a mixture of oximes on hydrolysis of benzoyl-α-furfuraldoxime.

This work has now been repeated and the origin of the difficulties of previous workers traced to the fact that the α-oxime in the presence of hot solvents is partly converted into the β-isomeride, a phenomenon never observed in the benzaldoximes. With care, a crystalline acetyl-α-furfuraldoxime can be prepared; this on hydrolysis gives nearly pure α-furfuraldoxime, which can also be obtained by hydrolysis of the benzoyl compound and isolation of the oxime by special means. β-Furfuraldoxime is obtainable under conditions which will not give β-benzaldoxime, being much more stable than that compound. The furfuraldoximes accordingly occupy an intermediate position between the benzaldoximes and the aliphatic aldoximes.

No oximes of the naphthalene series have been investigated from the point of view of the stereochemical hypothesis, so 2-methoxy-1-naphthaldoxime and 4-methoxy-1-naphthaldoxime have now been studied. The products of oximation have the α-aldoxime structure and we have been unable to convert either into the β-isomeride. As they may both be regarded as *o*-substituted benzaldoximes, this was not unexpected. On methylation of 2-methoxy-1-naphthaldoxime, a mixture of *N*- and *O*-ethers was obtained, the former predominating; 4-methoxy-1-naphthaldoxime gave a mixture of about equal amounts of *N*- and *O*-ethers. Both oximes therefore differ markedly from the α-benzaldoximes in the relative amounts of *N*- and *O*-ethers produced on methylation.

Experimental.

α-Furfuraldoxime.—Furfuraldehyde (13·5 g.) was added slowly to a cold mixture of sodium hydroxide (14 g. in 15 c.c of water) and hydroxylamine hydrochloride (12 g. in 30 c.c. of water). After 1 hour, the solution was filtered and cooled in a freezing mixture and a slight excess of an ice-cold, saturated aqueous solution of ammonium chloride was slowly added with stirring. The crystalline precipitate was washed with a little ice-cold water and air-dried. The yield of crude oxime (m. p. 51—64°) was 11·5 g. After crystallising three times from benzene and light petroleum, 4 g. of pure α-oxime were obtained, m. p. 75—76° (Goldschmidt and Zanoli, *loc. cit.*, give 73°). The details must be carefully followed, otherwise an inseparable mixture of the two isomerides may be obtained. In one experiment, a crude oxime, m. p. 42—45°, was obtained and repeated crystallisations failed to raise the melting point above 48—52°. It is probable that the material (m. p. 49—56°) obtained by Odernheimer (*loc. cit.*) was a similar mixture. When the pure

α-oxime (0·5 g.) was boiled with benzene (20 c.c.) under reflux for 4 hours and the solvent evaporated, a product, m. p. 47—48°, was obtained which was apparently a mixture of the α- and β-isomerides, since the addition of either raised its melting point.

Acetyl-α-furfuraldoxime.—α-Furfuraldoxime (2·5 g.) was slowly added to acetic anhydride (12 c.c.), and warmed to 30°; it then dissolved. On decomposing the excess of anhydride with 2*N*-sodium carbonate, crystals separated which were collected, air-dried, and dissolved in warm light petroleum; on cooling the solution to — 20° or — 40°, *acetyl-α-furfuraldoxime* separated in colourless prisms, m. p. 34—35° (Found: N, 9·4. $C_7H_7O_3N$ requires N, 9·2%). The acetyl derivative was warmed with 2*N*-sodium hydroxide until it dissolved; there was no odour of furfuronitrile. On cooling the solution, adding saturated ammonium chloride solution, extracting the mixture twice with ether, and evaporating the solvent with a current of air, an oxime was obtained which, after being pressed on a porous tile, melted at 69—72° and was nearly pure α-oxime. Goldschmidt and Zanoli (*loc. cit.*) obtained on acetylation an oil which on hydrolysis gave some furfuronitrile and an oxime, m. p. 49—60°.

Benzoyl-α-furfuraldoxime.—Crude α-furfuraldoxime, m. p. 51—57° (7 g.) was slowly added with cooling to benzoyl chloride (30 g.) and the product was poured into 2*N*-sodium hydroxide (250 c.c.), vigorously shaken for 30 minutes, and kept for 12 hours. The benzoyl derivative which separated was crystallised three times from alcohol; it then melted at 138—139° (compare Minunni, *loc. cit.*). The benzoyl derivative (5 g.) was heated with 2*N*-sodium hydroxide (50 c.c.), and the solution was cooled, saturated with carbon dioxide, and extracted with ether; removal of the solvent by a current of air gave a nearly pure α-oxime, m. p. 68—73°. It is essential that the solutions of the α-oxime should not be warmed, otherwise partial conversion into the β-oxime occurs.

β-*Furfuraldoxime.*—Hydroxylamine hydrochloride (10 g.) in methyl alcohol (40 c.c.) was treated with crystallised sodium acetate (19·5 g.) in dilute alcohol (40 c.c.), and furfuraldehyde (12 g.) added. The mixture was kept for 24 hours, the precipitated sodium chloride removed, and the solution evaporated in a vacuum at room temperature to about 30 c.c. and then poured into water (70 c.c.). The precipitated β-oxime (m. p. 89—91°) was crystallised three times from 10% alcohol with the addition of a little animal charcoal; a nearly quantitative yield was then obtained of the pure β-oxime, m. p. 91—92° (Goldschmidt and Zanoli give 89°). The β-oxime (2·5 g.) was dissolved in acetic anhydride (10 c.c.) at 30° and poured into 2*N*-sodium carbonate. When all the anhydride was decom-

posed, the oil was extracted with ether and hydrolysed, after removal of the solvent, by boiling it with 40% potassium hydroxide solution. Ammonia was evolved and extraction of the acidified solution with ether yielded pyromucic acid, identified by its reactions and by comparison with an authentic specimen.

α-2-*Methoxy*-1-*naphthaldoxime*.—To a mixture of hydroxylamine hydrochloride (7·5 g.) and sodium hydroxide (10 g.) in water (110 c.c.) was added a solution of 2-methoxy-1-naphthaldehyde (14 g.) in hot alcohol (20 c.c). The sodium salt of the oxime (which is very sparingly soluble in water) separated as a mass of crystals; after 1 hour, the oxime was liberated by addition of excess of a saturated solution of ammonium chloride, filtered off, washed, and dried (yield, almost quantitative). After three crystallisations from hot benzene, α-2-*methoxy*-1-*naphthaldoxime* formed white plates, m. p. 154—155° (Found: N, 7·3. $C_{12}H_{11}O_2N$ requires N, 7·0%).

α-*Acetyl*-2-*methoxy*-1-*naphthaldoxime*, prepared in the usual way, and crystallised from alcohol, formed white needles, m. p. 79—80° (Found: N, 5·9. $C_{14}H_{13}O_3N$ requires N, 5·8%). On hydrolysis with hot 2*N*-sodium hydroxide, the needles of the acetyl derivative are gradually replaced by the plates of the sodium salt of the oxime. On addition of ammonium chloride, the α-oxime was recovered unchanged.

α-2-*Methoxy*-1-*naphthaldoxime Hydrochloride*.—The oxime (2 g.) was dissolved in boiling chloroform (75 c.c.), and dry hydrogen chloride passed in for 20 minutes. The precipitated *hydrochloride* was collected, washed with chloroform, and pressed on a porous tile. It formed a bright yellow powder, m. p. 145—147° (decomp.) (Found: Cl, 16·4. $C_{12}H_{11}O_2N,HCl$ requires Cl, 14·9%). With sodium hydroxide and ammonium chloride, the hydrochloride regenerated the α-oxime; no inversion had taken place.

Methylation of α-2-*Methoxy*-1-*naphthaldoxime*.—The oxime (7·0 g.), dissolved in hot alcohol (85 c.c.), was treated with sodium ethoxide (1·05 g. of sodium in 25 c.c. of alcohol), and methyl iodide (5 g.) added. The solution was boiled under reflux for 30 minutes and kept for 12 hours, the alcohol allowed to evaporate somewhat, and excess of water added. An emulsion was formed, which was extracted first with ether, then with chloroform. The ethereal extract on evaporation gave a thick oil (2·4 g.) which solidified when cooled, yielding a hard, brown solid, m. p. 51—54°, consisting mainly of *O*-ether, but also containing a little *N*-ether, unchanged oxime, and other impurities. The *O*-ether is best separated by prolonged distillation in steam, in which it is difficultly volatile; it was identified in the distillate by comparison with an authentic specimen obtained by synthesis.

The chloroform extract gave a solid (4·6 g.), m. p. 106—107°. After some weeks, the m. p. had fallen to 83—87°. This compound on crystallisation from benzene gave pure *N-methyl-2-methoxy-1-naphthaldoxime hydrate*, fine needles, m. p. 88—89° (Found: N, 6·0; H_2O, 7·6. $C_{13}H_{13}O_2N,H_2O$ requires N, 6·0; H_2O, 7·7%). The anhydrous *N-methyl-2-methoxy-1-naphthaldoxime*, obtained by desiccation of the hydrate in a vacuum over calcium chloride, formed stout prisms, m. p. 118—119°, which hydrate readily (Found: N, 6·5. $C_{13}H_{13}O_2N$ requires N, 6·5%). Both the hydrated and the anhydrous ether yield *N*-methylhydroxylamine and 2-methoxy-1-naphthaldehyde on gentle boiling with acids.

α-*O-Methyl-2-methoxy-1-naphthaldoxime*.—2-Methoxy-1-naphthaldehyde (3·5 g.) and *O*-methylhydroxylamine (0·95 g.) were dissolved in alcohol (30 c.c.) and kept for 12 hours. The alcohol was allowed to evaporate spontaneously, and the dark solid residue purified by steam distillation and crystallisation from alcohol. α-*O-Methyl-2-methoxy-1-naphthaldoxime* formed colourless, short prisms, m. p. 65° (Found: N, 6·8. $C_{13}H_{13}O_2N$ requires N, 6·5%).

4-*Methoxy-1-naphthaldehyde*.—4-Hydroxy-1-naphthaldehyde (24 g.) was heated with potassium hydroxide (8 g. in 35 c.c. of water), and methyl sulphate (13 c.c.) added slowly with shaking. The mixture was heated on the water-bath for 30 minutes, potassium hydroxide (5·5 g. in 20 c.c. of water) and methyl sulphate (8 c.c.) were then added alternately in small quantities with shaking. Heating was continued for 30 minutes, and the solution was cooled and extracted with ether. The aqueous portion on acidification gave 4·8 g. of impure 4-hydroxy-1-naphthaldehyde. The ethereal portion was well washed with dilute sodium hydroxide solution, then with water, dried, and evaporated. The yield of crude methoxyaldehyde, which was sufficiently pure for the next operation, was 10·8 g. A considerable quantity of tar was formed. 4-Methoxy-1-naphthaldehyde has previously been prepared by boiling 4-hydroxy-1-naphthaldehyde with methyl iodide and potassium hydroxide in alcoholic solution (Gattermann, *Annalen*, 1907, **357**, 365).

α-*4-Methoxy-1-naphthaldoxime*, prepared from the crude aldehyde in a similar way to the 2-methoxy-compound, crystallised from benzene in white needles, m. p. 107—108° (Found: N, 7·3. $C_{12}H_{11}O_2N$ requires N, 7·0%).

α-*Acetyl-4-methoxy-1-naphthaldoxime*, prepared in the usual way, crystallised from alcohol in colourless needles, m. p. 102° (Found: N, 5·8. $C_{14}H_{13}O_3N$ requires N, 5·8%). On warming it with 2*N*-sodium hydroxide and saturating the solution with carbon dioxide, the original α-oxime was obtained.

α-*4-Methoxy-1-naphthaldoxime hydrochloride*, prepared in the

same way as the corresponding 2-methoxy-compound, formed a yellowish-green powder, m. p. 144—145° (decomp.) (Found: Cl, 15·1. $C_{12}H_{11}O_2N$,HCl requires Cl, 14·9%). On decomposing it with 2*N*-sodium carbonate, the original oxime was regenerated.

Methylation of α-4-*Methoxy*-1-*naphthaldoxime*.—The oxime (6·55 g. in 59 c.c. of alcohol), sodium (0·8 g. in 20 c.c. of alcohol), and methyl iodide (5·1 g. in 20 c.c. of alcohol) were boiled under reflux for 20 minutes and kept for 12 hours. The methylated product was worked up in the same way as the 2-methoxy-oxime, there being obtained 3·1 g. of *O*-methyl ether and 3·0 g. of *N*-methyl ether. α-O-*Methyl*-4-*methoxy*-1-*naphthaldoxime* formed colourless needles, m. p. 38—39°, from alcohol and water (Found: N, 6·5. $C_{13}H_{13}O_2N$ requires N, 6·5%). α-N-*Methyl*-4-*methoxy*-1-*naphthaldoxime* is dimorphic and separated from hot benzene in yellow prisms, m. p. 158—159° (Found: N, 6·4%), which changed to dark grey plates on keeping in contact with the mother-liquor for 2 hours. The grey modification passed back into the yellow on crystallisation or on heating at 100° for some time.

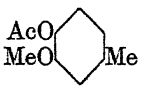
THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, June 15th*, 1927.]

CCLVI.—*Nitro-derivatives of the Homopyrocatechol Ethers.*

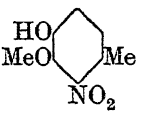
By ALBERT EDWARD OXFORD.

IT has previously been shown (Oxford, J., 1926, 2004) that the action of acetyl nitrate on *o*-methoxyphenyl acetate at −15° gives rise to 3-nitro- and 5-nitro-2-methoxyphenyl acetates in about equal quantities. It was hoped that the application of this method to *m*-methoxy-*p*-tolyl acetate (I) would yield a relatively considerable proportion of the 2-nitro-derivative and provide a new and more direct route to 2-nitrohomoveratrole, although it was, of course, recognised that the effect of the methyl group would be to suppress substitution in the position between it and the methoxyl group (compare the nitration of aceto-*m*-toluidide, Cohen and Dakin, J., 1903, **83**, 331; and of *m*-cresol, Gibson, J., 1923, **123**, 1269). In point of fact, the effect was such that the yield of the 2-nitro-derivative could not be raised above 5%, although nearly every possible variation in the experimental conditions was tried, including a nitration at −40°. The method did, however, provide a means of preparing the hitherto unknown nitro-derivatives of creosol and homoveratrole, *viz.*, 2-*nitrocreosol* (II), 2 : 5-*dinitrocreosol* (III)

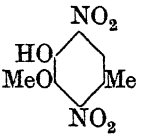
(readily obtained by nitrating II in acetic acid solution), and 2 : 5-*dinitrohomoveratrole* (IV).



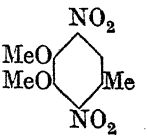
(I.)



(II.)



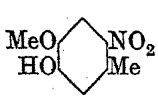
(III.)



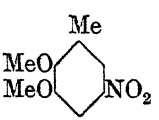
(IV.)

In view of the interest attaching to 2-nitrohomoveratrole (see Oberlin, *Arch. Pharm.*, 1925, **263**, 641; Gulland and Robinson, J., 1926, 1976; compare also Dadswell and Kenner, this vol., p. 580), and of the strong probability that, like homoveratrole and 2-nitro-*m*-tolyl methyl ether, it should be a solid at the ordinary temperature, a method for its complete separation from 6-nitrohomoveratrole was much needed. It was found that under conditions of alkaline hydrolysis which leave the 2-nitro-isomeride unaffected, 6-nitrohomoveratrole is quantitatively demethylated to 6-nitro*iso*creosol (V), and a specimen of 2-nitrohomoveratrole prepared from 2 : 6-dinitrohomoveratrole according to Oberlin's details, after being submitted to this treatment, was found to contain only a trace of 6-nitrohomoveratrole. The purified 2-nitrohomoveratrole could then for the first time be obtained crystalline, having m. p. 6—7·5°. Apparently sodium sulphide (the reducing agent used by Gulland and Robinson, whose final product was undoubtedly a mixture of the two nitrohomoveratroles) attacks both nitro-groups in 2 : 6-dinitrohomoveratrole, whilst ammonium sulphide (the reducing agent used by Oberlin), being milder and more specific in its action, reduces only the 6-nitro-group.

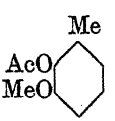
In conclusion, some comparative experiments have been carried out in the *o*-creosol series. The nitration of *o*-homoveratrole by concentrated nitric acid yields only the 5-nitro-derivative (VI) (Cain and Simonsen, J., 1914, **105**, 156; Majima and Okazaki, *Ber.*, 1916, **49**, 1482), and the same result is obtained if acetyl



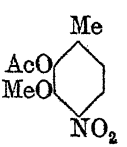
(V.)



(VI.)



(VII.)



(VIII.)

nitrate at −15° is the nitrating agent. The nitration of 3-methoxy-*o*-tolyl acetate (VII) under conditions which convert *o*-methoxyphenyl acetate into its 5-nitro-derivative only, yields chiefly the 4-nitro-derivative (VIII) and not, as might be expected, the 6-nitro-derivative.

Experimental.

Nitration of m-*Methoxy*-p-*tolyl Acetate* (I).—A mechanically stirred solution of the acetate (32·2 g.) and redistilled acetyl chloride (35 c.c.) in pure dry carbon tetrachloride (140 c.c.), cooled in a freezing mixture and protected from moisture, was treated during 2½ hours with dry, very finely powdered silver nitrate (36 g.). The 6-nitro-derivative began to crystallise just before all the silver nitrate had been added. Stirring was continued for a further hour, the reaction mixture filtered, and the precipitate—which contained the greater part of the 6-nitro-derivative mixed with silver salts—washed with carbon tetrachloride. The deep red filtrate was shaken twice with water, dried over anhydrous sodium sulphate, and, after evaporation of the solvent, distilled in a vacuum, three fractions being collected : (i) (Up to 167°/13 mm.) 5 g. of a red liquid; (ii) (167—177°/13 mm.) 8 g., mostly liquid; (iii) (177—210°/13 mm.) 5 g. of a solid (6-nitro-3-methoxy-*p*-tolyl acetate); (i) and the liquid part of (ii) were combined and hydrolysed by warming on the steam-bath with 2*N*-sodium hydroxide.

6(?)-*Chlorocreosol*.—The crude phenolic mixture was steam-distilled; the brown, semi-solid material (about 4 g.) that came over, after repeated crystallisation from water, was obtained in colourless, glistening, rectangular leaflets, m. p. 71° (Found : Cl, 19·7; *M*, in camphor, 174. $C_8H_9O_2Cl$ requires Cl, 20·5%; *M*, 172). It is sparingly soluble in cold water and dissolves readily in all organic solvents with the exception of light petroleum. It has a faint, guaiacol odour, gives no coloration with ferric chloride, and does not dissolve chemically in sodium bicarbonate solution.

Its *acetyl* derivative crystallises from light petroleum in colourless, thick tablets, m. p. 61° [Found : MeO (micro-Zeisel), 14·2. $C_{10}H_{11}O_3Cl$ requires MeO, 14·5%]. It is readily soluble in ethyl and methyl alcohols and moderately easily soluble in hot water.

The *methyl ether*, obtained by the xylene–methyl sulphate–potassium carbonate method, crystallises from aqueous alcohol in colourless, shining leaflets, m. p. 37—38°. It has an almost ethereal odour recalling that of *m*-methoxy-*p*-tolyl acetate, and gives a yellow coloration with concentrated sulphuric acid. In order to decide which position (2 or 6) is occupied by the chlorine atom, the behaviour of this ether on nitration was investigated. It dissolved in concentrated nitric acid to a red solution, from which nothing was precipitated by addition of water at the end of 10 minutes, but when nitrated in acetic anhydride solution at 0°, by concentrated nitric acid, it yielded a minute amount of a brown solid which crystallised from light petroleum in colourless, well-defined prisms, m. p. 89°. The amount of this substance obtained

was insufficient for further investigation, but the behaviour of the chlorocreosol towards nitrating agents recalls that of 6-nitrohomoveratrole and is quite unlike that of 2-nitrohomoveratrole, which is readily nitrated to 2 : 6-dinitrohomoveratrole.

2-*Nitrocreosol* (II).—The nitrocreosols remaining in the distillation flask after the removal of chlorocreosol * were extracted with ether, and after evaporation of the solvent a dark oil remained, the solution of which in boiling light petroleum (b. p. 60—80°) deposited, on cooling, 6-nitrocreosol mixed with a little tar. After evaporation of the mother-liquor, a yellow oil remained (1·5 g.) which proved to be fairly pure 2-nitrocreosol. It was again heated with a little light petroleum, and the undissolved oil (1 g.), which would not crystallise at — 15°, was used in the experiments described below.

2-*Nitro*-3-*methoxy*-4-p-*nitrobenzyloxytoluene*.—The benzoyl derivative of 2-nitrocreosol was an uncrystallisable oil, and the phenol had to be characterised by the preparation of its p-*nitrobenzyl ether*. 2-Nitrocreosol (1·6 g., a slight excess) together with *p*-nitrobenzyl bromide (1·83 g.) was dissolved in a solution of sodium (0·19 g.) in absolute alcohol (60 c.c.), and the whole boiled under reflux for 3½ hours; much water was then added. The precipitate (m. p. 100°) obtained, after five crystallisations from alcohol, separated in fern-like aggregates of minute, colourless, flat rods, m. p. 114—114·5°, unaltered by further crystallisations from alcohol or light petroleum (Found : N, 9·1, 8·9. $C_{15}H_{14}O_6N_2$ requires N, 8·8%). It is readily soluble in most organic solvents.

6-*Nitro*-3-*methoxy*-4-p-*nitrobenzyloxytoluene* was prepared from 6-nitrocreosol by an exactly similar method. It was crystallised from hot alcohol, in which it was very sparingly soluble, and then from benzene, separating in pale yellow, feathery needles, m. p. 202—203° (Found : C, 56·1; H, 4·8. $C_{15}H_{14}O_6N_2$ requires C, 56·6; H, 4·4%).

2 : 5-*Dinitrocreosol* (III).—2-Nitrocreosol (2·6 g.) dissolved in glacial acetic acid (9 c.c.) was nitrated by the addition of a solution of nitric acid (*d* 1·42; 3·5 c.c.) in glacial acetic acid (3 c.c.) with constant stirring and cooling in ice-water, the first half of this solution being added during 10 minutes and the rest during 1 minute. Water was added immediately and the product was collected, washed, and dried (yield, 0·67 g., *i.e.*, 25% of the theoretical). It separated from light petroleum (b. p. 40—60°) in yellow leaflets, m. p. 86—87°, not altered by a second crystallisation from that solvent, from which it was also deposited in flat needles

* By substituting acetic anhydride for the excess of acetyl chloride used in the nitration, the formation of chlorocreosol can largely be suppressed; the yield of 2-nitrocreosol is, however, if anything diminished.

by rapid crystallisation from a saturated solution (Found : N, 12·1. $C_8H_8O_6N_2$ requires N, 12·3%). It is readily soluble in hot, but only sparingly soluble in cold water, dissolves in aqueous sodium carbonate to a red solution, and gives no coloration with ferric chloride.

Its *acetyl* derivative, obtained by boiling the phenol with excess of acetic anhydride for several hours, crystallises from light petroleum in flat rods, m. p. 53—54°. It is readily soluble in alcohol and gives a pale yellow colour with concentrated sulphuric acid.

The aqueous mother-liquor from the nitration of 2-nitrocreosol was made alkaline with caustic soda, then neutralised with dilute sulphuric acid and extracted with ether. A solid remained after evaporation of the solvent which, when repeatedly crystallised from light petroleum, eventually yielded pure 5 : 6-dinitrocreosol. This observation proves that the 2-nitrocreosol originally used contained a considerable proportion of the 6-nitro-isomeride.

2 : 5-*Dinitrohomoveratrole* (IV).—2 : 5-Dinitrocreosol (0·45 g.) dissolved in dry xylene (7 c.c.) was boiled under reflux with methyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.). After 30 minutes, a further 0·2 c.c. of methyl sulphate was added, and the liquid was boiled for a further 20 minutes and then worked up in the usual way. When the crude product was distilled, four drops of a nearly colourless oil came over at 190°/15 mm. Its solidification was effected by first cooling in solid carbon dioxide, when it set to a glass, and then transferring it to an ice–salt mixture and scratching vigorously; almost immediate crystallisation then set in.* The solid was obtained in colourless, six-sided plates, m. p. 36°, after two crystallisations from aqueous alcohol (Found : N, 11·5. $C_9H_{10}O_6N_2$ requires N, 11·6%). It gives a pale yellow colour with concentrated sulphuric acid, and the diamine it yields on reduction will not condense with phenanthraquinone to a derivative of phenazine.

2-*Nitrohomoveratrole from* 2-*Nitrocreosol*.—Distillation in steam, followed by repeated fractional distillation in a vacuum, provides a fairly efficient means of separating the two nitrohomoveratroles. The nitrocreosols remaining after all the chlorocreosol had been removed (see p. 1966) were therefore methylated (preferably with methyl iodide) and the methyl ethers were isolated and submitted to steam distillation until the liquid distilling over no longer con-

* This method was applied with equal success to the purified 2-nitrohomoveratrole (see p. 1965) and to 3-nitro-2-methoxyphenyl acetate (Oxford, *loc. cit.*), an oil which had also previously resisted all attempts at crystallisation. This acetate separates from slightly aqueous alcohol in colourless, well-defined, hexagonal tablets, m. p. 29—30°.

tained any trace of oily drops. 6-Nitrohomoveratrole is appreciably volatile in steam (to the extent of 0·5 g. per litre), although much less so than its isomeride. The distillate was kept for several days in the ice-chest, filtered from 6-nitrohomoveratrole, and extracted with ether. A further separation of the two isomerides by repeated fractional distillation in a vacuum is possible, 2-nitrohomoveratrole being slightly the more volatile (Found in the best fraction: C, 54·9; H, 5·6. Calc. for $C_9H_{11}O_4N$: C, 54·8; H, 5·6%). The proportion of 2-nitrohomoveratrole in a given fraction can roughly be estimated by nitration to 2 : 6-dinitrohomoveratrole under the following conditions: The oil (about 1 g.) is nitrated by stirring with nitric acid (*d* 1·42; 3 c.c., previously boiled) for 2·5 minutes (cooling by means of running water). Much water is then added and the precipitate, after standing for a while, is collected in a Gooch crucible, dried, and weighed. Under these conditions, 6-nitrohomoveratrole gives only a 9·7% yield of somewhat impure 5 : 6-dinitrohomoveratrole. Three different specimens of 2-nitrohomoveratrole, prepared from impure 2-nitrocreosol and purified as outlined above, were found to contain at the least 77%, 80%, and 66% of that constituent respectively. On further nitration, they all gave specimens of almost pure 2 : 6-dinitrohomoveratrole with m. p. 85—89° instead of 90—91°.

5 : 6-*Dinitrohomoveratrole*.—According to Oberlin (*loc. cit.*), the direct nitration of 6-nitrohomoveratrole by fuming nitric acid below 5° gives 5 : 6-dinitrohomoveratrole in 36% yield. The present author found the yield could be increased to 60% by allowing a solution of 6-nitrohomoveratrole (0·7 g.) in acetic anhydride (5 c.c.) mixed with nitric acid (*d* 1·42; 1 c.c.) to stand for ½ hour, the temperature being maintained at 0°.

6-*Nitro*isocreosol (V).—6-Nitrohomoveratrole (6 g.) was boiled under reflux during 28 hours with a solution of caustic potash (23 g.) in water (150 c.c.). A further quantity of caustic potash solution (6 g. in 25 c.c. of water) was then added, and the boiling continued for a further 9 hours until 6-nitrohomoveratrole could no longer be seen in the condenser. On cooling, the deep red liquid deposited slender, orange needles of the potassium salt of the nitro*iso*creosol. Sufficient water was added to dissolve the crystals, and on addition of dilute sulphuric acid nearly pure 6-nitro*iso*creosol was precipitated. It was crystallised from very dilute hydrochloric acid (charcoal) and then from benzene, from which it separated in long, slender, pale yellow needles, m. p. 168—170°. The nitro-*iso*creosol, m. p. 166—167°, isolated in small amount by Gulland and Robinson (*loc. cit.*) in some experiments on the nitration of *iso*creosol in ethereal solution, must therefore be the 6-nitro-deriv-

ative (Found : C, 52·7; H, 4·9. $C_8H_9O_4N$ requires C, 52·5; H, 4·9%).

6-Nitro*iso*creosol is readily soluble in alcohol and ethyl acetate, moderately easily soluble in chloroform in the cold, and very sparingly soluble in cold benzene and carbon tetrachloride. Its golden-orange solution in saturated aqueous sodium carbonate deposits the bright yellow *sodium* salt on addition of concentrated sodium hydroxide. It gives no coloration with ferric chloride.

Its constitution was proved by methylation to 6-nitrohomoveratrole, the methylation being almost complete after 2 hours' boiling with methyl sulphate, xylene, and potassium carbonate.

The *acetyl* derivative was obtained by boiling the nitrophenol with excess of acetic anhydride for 2 hours. It crystallises from alcohol in pale yellow leaflets, m. p. 98—98·5°, and gives a deep red coloration with concentrated sulphuric acid.

Separation of the Two Nitrohomoveratroles.—When a mixture of about equal quantities of 2- and 6-nitrohomoveratroles is demethylated under the foregoing conditions, the oil remaining unattacked contains less than 5% of 6-nitrohomoveratrole. If the original mixture consists largely of 2-nitrohomoveratrole, the removal of the 6-nitro-isomeride is complete. The accumulated mother-liquors from which crude 6-nitro*iso*creosol had been precipitated by acidification were extracted with ether, and the residue remaining after the evaporation of the solvent was submitted to distillation in steam in the hope of isolating 2-nitro*iso*creosol, but the distillate contained only 6-nitro*iso*creosol, which is slightly volatile in steam.

6-*Bromo*-2-*nitrohomoveratrole.*—Bromine (6 g.; 1½ equivs.) was added drop by drop with shaking to a solution of 2-nitrohomoveratrole (4·8 g.; 1 equiv., prepared from 2 : 6-dinitrohomoveratrole by Oberlin's method, but not further purified by the alkali treatment) in glacial acetic acid (10 c.c.). Considerable heat was developed. The liquid was kept at room temperature for 48 hours, a considerable proportion of the bromo-derivative crystallising, and then shaken with a large volume of sodium bisulphite solution. The precipitate, after being thoroughly washed with water and dried (yield, 5·8 g. or 86% of the theoretical; m. p. 99—100°), crystallised from methyl alcohol in large, colourless, four-sided tablets, m. p. 102—103° (Found : Br, 28·5. $C_9H_{10}O_4NBr$ requires Br, 29·0%) and was readily soluble in all the usual organic solvents with the exception of cold methyl and ethyl alcohols, and light petroleum, in which it was moderately easily soluble when hot and very sparingly soluble in the cold.

5 : 6-*Dinitroisocreosol.*—A solution of the acetyl derivative of 6-nitro*iso*creosol (0·6 g.) in ice-cold nitric acid (*d* 1·5; 3·5 c.c.)

was kept at 0° for 3 hours. Water was then added, and the precipitate collected, washed, and dried (0·2 g.). The filtrate became deep red on the addition of alkali, hence considerable demethylation had taken place. The crude acetyl derivative crystallised from aqueous alcohol in colourless, flat needles, m. p. 109—110°. It was then hydrolysed by warming with sodium carbonate solution and alcohol on the steam-bath. The crude nitrophenol, precipitatated by the addition of hydrochloric acid, was recrystallised from water several times, forming very pale yellow, minute, slender needles, m. p. 128—129° (Found : N, 12·3. $C_8H_8O_6N_2$ requires N, 12·3%). It is readily soluble in alcohol, moderately easily soluble in cold benzene, and sparingly soluble in light petroleum and cold carbon tetrachloride. Its orange-coloured solution in saturated aqueous sodium carbonate deposits orange-yellow, flat, pointed rods of the *sodium* salt on addition of concentrated caustic soda. It gives a brownish-red coloration with alcoholic ferric chloride. Its constitution follows from the fact that it yields 5 : 6-dinitrohomoveratrole (m. p. 119—120°) on methylation.

Nitration of 3-*Methoxy*-o-*tolyl Acetate* (VII).—This was carried out according to the details given by Graesser-Thomas, Gulland, and Robinson (J., 1926, 1973) for the preparation of 6-nitro-*m*-methoxy-*p*-tolyl acetate (method B). A solution of nitric acid (1·8 c.c.; *d* 1·4) in acetic anhydride (2 c.c.) to which a few small crystals of urea had been added was very slowly introduced, drop by drop, into a mixture of the acetate (2·5 g.) and acetic anhydride (2·5 c.c.) cooled to — 15°. Addition of water after 15 minutes precipitated an oil, which was hydrolysed by warming it on the steam-bath with *N*-caustic soda. Acidification with dilute sulphuric acid then precipitated an oil; this, after a tedious treatment with light petroleum followed by two crystallisations from water, yielded a minute quantity of a substance, m. p. 60—61°, which crystallised from water in colourless, silky needles, gave no coloration with ferric chloride, and dissolved in saturated sodium carbonate to a golden-yellow solution. It was probably 4-nitro-*o*-creosol, since it yielded a nitrophenol when nitrated in acetic acid solution, the aminophenol from which condensed with phenanthraquinone to give a derivative of phenazine which gave a dull cherry-red colour with concentrated sulphuric acid and exhibited a perceptible green fluorescence in benzene solution (compare the behaviour of 3 : 4-dinitroguaiacol; Oxford, *loc. cit.*).

The various aqueous mother-liquors from the foregoing operations were extracted with ether, the extract was added to the light petroleum mother-liquors, and the residue remaining after evaporation of the combined extracts was methylated by the xylene-

methyl sulphate–potassium carbonate method. The methyl ethers were nitrated by heating them on the steam-bath for 10 minutes with a considerable excess of fuming nitric acid diluted with an equal volume of glacial acetic acid. Addition of water then precipitated almost pure 4 : 5-dinitro-*o*-homoveratrole, m. p. 125—127° after one crystallisation from alcohol (Majima and Okazaki, *loc. cit.*, record m. p. 126—127°). Further proof of the position of the nitro-groups was afforded by condensing the diamine obtained by reduction with zinc and hydrochloric acid, with phenanthraquinone; a substance exhibiting all the colour reactions of a 1 : 2-dimethoxyphenanthraphenazine was then obtained.

I wish to thank Professor R. Robinson, F.R.S., for his continued interest in this work and for many helpful suggestions during its progress.

THE UNIVERSITY, MANCHESTER. [*Received, June 11th*, 1927.]

CCLVII.—*Nitration of β-Naphthyltrimethylammonium Nitrate.*

By BERTRAM HOBART INGHAM.

IT has been shown by Vorländer and Sieberts (*Ber.*, 1919, **52**, 283) that in simple benzene derivatives the positively charged ammonium group in immediate proximity to the nucleus has an almost exclusive meta-orienting effect. This is a particular example of the generalisation, first enunciated by Robinson, that a positively charged group in immediate proximity to the nucleus always conduces to the formation of a high proportion of meta-substitution products. The former authors showed that on nitration of phenyltrimethylammonium nitrate or bromination of the bromide the corresponding meta-derivatives were produced, whilst *o*-, *m*-, and *p*-tolyltrimethylammonium nitrates yield, on nitration, 5-nitro-2-tolyl-, 4-nitro-3-tolyl-, and 3-nitro-4-tolyl-ammonium nitrates respectively. The so-called "effect" of this group is therefore strongly opposed to that of hydroxyl or methoxyl. In β-naphthol and its methyl ether the positions most readily substituted are precisely those which may be deduced from the simplest application of the rule of alternation, namely 1, 8, 6, and 3, and on such grounds it must be inferred that substitution at these positions in β-naphthyltrimethylammonium salts will occur less readily than in the corresponding positions in naphthalene itself. The simple rules of alternation, however, give no clue as to which of the remaining positions, namely, 7, 5, or 4, will be most readily attacked. It is well known that, in the

naphthalene series, substitution occurs preferentially in the α-positions, and therefore positions 5 and 4 are more probable points of substitution than position 7. There remains yet a choice to be made between positions 5 and 4. If the action of the "meta-directive" group is to assist in the process of substitution in any way, then, other things being equal, the nucleus containing the directive group should be the more susceptible to substitution (as is the case with the two naphthols, for example). On the contrary, if its influence be inhibitory, and if the inhibition applies not only to the ortho- but also to the meta-position (to a smaller extent), then such influence should be most effective in the nucleus to which the group is attached, and position 5, being less affected than position 4, should be the more susceptible to substitution.

The author's experiments emphatically support the latter view, which, moreover, is entirely consistent with the results obtained in the schools of H. E. Armstrong and of A. F. Holleman. The product obtained on nitration of β-naphthyltrimethylammonium nitrate was nearly pure 5-nitro-β-naphthyltrimethylammonium nitrate in almost theoretical yield.

EXPERIMENTAL.

β-Naphthyltrimethylammonium iodide was prepared by a method similar to those of Bamberger (*Ber.*, 1889, **22**, 1306) and of Morgan (J., 1900, **77**, 882), but it was found to be unnecessary to heat the reactants in a sealed tube, refluxing for 3½ hours (in a copper flask) and allowing the crude product to stand over-night before purification being found to give practically as good a yield (approx. 60%). The substance was purified by extraction with and crystallisation from water, followed by recrystallisation from alcohol; it was thus obtained in colourless, hexagonal plates, m. p. 193° (decomp.).

The *nitrate* and the *picrate* were obtained by double decomposition from the iodide with silver nitrate and with picric acid, respectively; they crystallised from water, the nitrate in colourless, rectangular plates, m. p. 190° (decomp.), and the picrate in golden-yellow needles, m. p. 194—195° (decomp.).

Nitration of β-Naphthyltrimethylammonium Nitrate.—The salt was dissolved in three times its weight of 99% nitric acid (*d* 1·52) with water-cooling, a vigorous momentary reaction taking place. After having stood at room temperature for 2 hours, the solution was poured on 1½—2 times its weight of ice, and the product made almost neutral * with (solid) sodium bicarbonate, separation of the

* The substance acts as its own indicator, any alkalinity (even that of sodium bicarbonate) producing an intense red colour.

nitro-compounds proceeding with the neutralisation. The yield was almost theoretical. After two crystallisations from water and one from aqueous alcohol, a *mononitro-β-naphthyltrimethylammonium nitrate* was obtained in orange-yellow, rectangular prisms, m. p. 231° (decomp.) (Found: C, 52·5; H, 5·6; N, 14·4. $C_{13}H_{15}O_5N_3$ requires C, 53·2; H, 5·1; N, 14·3%). The nitrate was homogeneous, for when it was subjected to fractional crystallisation and subsequent conversion into the iodide, followed by refractionation, no difference in melting point or in appearance under a polarising microscope of any of the fractions could be detected.

The *iodide* was obtained from water in golden-yellow, rectangular prisms, m. p. 194° (decomp.) (Found: I, 35·9. $C_{13}H_{15}O_2N_2I$ requires I, 35·5%). The *picrate* was obtained from aqueous acetone in canary-yellow, rectangular prisms, softening from 248°, m. p. 254° (decomp.).

Unsuccessful attempts were made to determine the constitution of this nitration product of β-naphthyltrimethylammonium nitrate by oxidation, and also by treatment with concentrated aqueous solutions of alkalis, which caused the substance to undergo a peculiar and complicated change. In the circumstances, it was decided to proceed by synthesis as described below.

Methylation of 5-Nitro-β-naphthylamine.—5-Nitro-β-naphthylamine (Friedländer and St. Szymanski, *Ber.*, 1892, **25**, 2076) (1 mol.) in benzene (15 parts by weight) and methyl sulphate (4 mols.) in benzene (4 parts) were mixed and refluxed for 6½ hours, a dirty-white solid gradually separating. Next day, the precipitate was collected, washed with benzene, and boiled with water (100 parts), and the aqueous extract was cooled and made alkaline with ammonia, whereby the methylated bases were precipitated. The filtered solution, which contained 5-nitro-β-naphthyltrimethylammonium methosulphate, was divided into two portions, one of which was converted into the *iodide* (Found by micro-analysis: N, 8·4. $C_{13}H_{15}O_2N_2I$ requires N, 7·8%) and the other into the *picrate* by means of sodium iodide and picric acid, respectively.

Comparative and mixed m. p. tests showed that the nitration product of β-naphthyltrimethylammonium nitrate was 5-nitro-β-naphthyltrimethylammonium nitrate (see table).

As the yield of the quaternary salt obtained in the methylation experiment was very small, and also for comparative purposes, it was considered desirable to methylate the 8-nitro-isomeride and thereby furnish conclusive proof that the above quaternary salt was derived from 5-nitro-β-naphthylamine, and not from any impurity in it. The methylation was performed in the same way as that of the 5-isomeride.

Melting points of Nitro-β-naphthyltrimethylammonium Salts.

	5-Iso-meride.	8-Iso-meride.	Corresponding salt (X) from nitration product.	5-Iso-meride mixed with X.	8-Iso-meride mixed with X.
Iodide (1st sample)	189°	180°	192°	190°	180°
(2nd sample)	190	—	191	191	—
Picrate (1st sample)	254*	221—223	254*	254*	212—218
(2nd sample)	254*	221—223	254*	254*	212—229

* With softening from approximately 248° in each case.

The discrepancies of one or two degrees between some of the melting points given in the table and those of the corresponding substances given hitherto are due to the rate of heating; the m. p.'s in the table are strictly comparable, for they were taken simultaneously in the same bath.

The author wishes to express his thanks to Professor Lapworth for his interest in the investigation.

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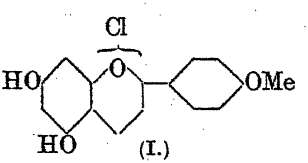
CCLVIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XII.*

By DAVID DOIG PRATT, ALEXANDER ROBERTSON, and ROBERT ROBINSON.

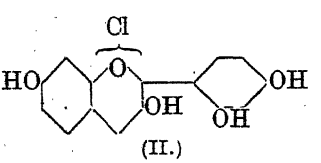
WHEN acacetinidin chloride (I) (Part IV, Pratt, Robinson, and Williams, J., 1924, **125**, 200) was demethylated, it yielded a very well-characterised trihydroxyflavylium chloride which had the reactions but not the crystalline form of apigeninidin chloride prepared by demethylation of its trimethyl ether (Part VI, J., 1925, **127**, 1133). The properties of the two specimens were closely similar, but not identical in every respect, and for this reason there was a doubt in regard to the course of the condensation of benzoylacetaldehyde and its derivatives with phloroglucinol in the presence of hydrogen chloride. Hitherto no unmethylated phloroglucinaldehyde derivative could be condensed with ketones of the form $CH_3 \cdot CO \cdot R$ to flavylium salts, but we have now found that *O*-benzoylphloroglucinaldehyde (this vol., p. 1713) can be utilised for this purpose. With *p*-methoxyacetophenone, it gives a benzoylacacetinidin chloride, and, after hydrolysis with methyl-alcoholic ammonia and subsequent treatment with hydrochloric acid, acacetinidin chloride, identical with the salt already described, was obtained. There is, therefore, no doubt that the condensation of anisoylacet-

aldehyde and phloroglucinol proceeds normally and does not, as was at one time suspected, give rise to an *epi*flavylium derivative. The specimen of apigeninidin chloride, prepared as described in this communication, is unquestionably more pure than that which was obtained previously by demethylation of the trimethyl ether. These results have been confirmed in the chrysinidin series and one and the same chrysinidin has been obtained on the one hand by the condensation of benzoylacetaldehyde and phloroglucinol, and on the other by hydrolysis of the benzoylchrysinidin chloride derived from *O*-benzoylphloroglucinaldehyde and acetophenone.

The condensation of benzoylacetaldehyde with acetophenone by means of hydrogen chloride in acetic acid solution was first described by Bülow and Sicherer (*Ber.*, 1901, **34**, 3896). The quantity of acetic acid employed was not stated, but the red product, $C_{15}H_{13}O_4Cl$, was very sparingly soluble in organic solvents and soon separated from the reaction mixture. These authors do not mention the necessity for any special precautions in carrying out the process, and in the first attempts which we made to repeat it the product was invariably an ochre-red, very sparingly soluble substance which separated quickly in almost quantitative amount. This substance can be easily prepared by adding phloroglucinol and benzoylacetaldehyde in molecular proportion to formic acid or by adding a few drops of hydrochloric acid to an acetic acid solution of the components. It appears to have the composition $C_{30}H_{22}O_7$ and, on treatment with a boiling mixture of acetic and hydrochloric acids, it slowly passes into chrysinidin chloride. Later it was found that the Bülow condensation could be effected in ethereal solution, and also in acetic acid solution if the materials were free from water and access of moisture to the reaction mixture was prevented. In the latter case, the dark reddish-brown product had the composition $C_{15}H_{11}O_3Cl$ and only began to separate after some hours. An account of the preparation of resomorinidin chloride (II) is included in this communication.



(I.)



(II.)

EXPERIMENTAL.

Trianhydrobisbenzoylacetaldehydephloroglucinol. — Cold filtered solutions of benzoylacetaldehyde (2·9 g.) in formic acid (5 c.c.) and of phloroglucinol (2·5 g.) in formic acid (40 c.c.) were mixed; an orange-red product soon began to separate. After 2 hours,

water was added and the substance was collected, washed, and dried at 100° (Found: C, 72·9, 73·2; H, 4·5, 4·6. $C_{30}H_{22}O_7$ requires C, 72·8; H, 4·5%). The yield was 5·1 g., and only when relatively more phloroglucinol was employed could the phenol be detected in the filtrate. The substance can also be obtained by addition of a few drops of hydrochloric acid to a solution of the components in equimolecular proportion in acetic acid or by passing hydrogen chloride into an acetic acid solution of benzoylacetaldehyde and phloroglucinol without precautions aimed at the exclusion of water. Attempts to crystallise this very sparingly soluble compound were unsuccessful. On heating, the substance darkens slightly from 210—280° and above this temperature gradually chars without melting.

Chrysinidin Chloride (5 : 7-*Dihydroxyflavylium Chloride*).—(A) The product of condensation of benzoylacetaldehyde and an equivalent amount of anhydrous phloroglucinol in ethereal solution by means of hydrogen chloride in the cold during 4 hours was collected and extracted with boiling dilute hydrochloric acid. The salt crystallised from the hot filtrates (poor yields) in reddish-brown prismatic needles, which were dried over sulphuric acid (Found: C, 58·7; H, 4·7. $C_{15}H_{11}O_3Cl,2H_2O$ requires C, 58·1; H, 4·8%). This salt darkens at 250° but does not melt at 300°. Its yellow solution in concentrated sulphuric acid does not fluoresce, nor do the orange-red alcoholic solutions exhibit this property. The salt is sparingly soluble in aqueous hydrochloric acid (even 0·05%) and dissolves in aqueous sodium carbonate to a deep brownish-red solution which is orange in thin layers. Sodium hydroxide gives the same colour, but the solutions soon become orange, especially on heating.

(B) A solution of the salt was obtained by boiling the orange-red compound, $C_{30}H_{22}O_7$, for 6 hours with an excess of a mixture of acetic acid (2 vols.) and concentrated hydrochloric acid (1 vol.). Water was added, and the perchlorate precipitated from the filtered solution.

(C) A solution of anhydrous phloroglucinol (5 g.) and benzoylacetaldehyde (8 g.) in pure glacial acetic acid (35 c.c.) was saturated with hydrogen chloride in an apparatus designed to exclude moist air, and then kept for 12 hours. The deep reddish-brown crystals which slowly separated were collected, washed with acetic acid, and dried over sodium hydroxide in a vacuum (Found: C, 65·6, 65·4; H, 4·4, 4·1. $C_{15}H_{11}O_3Cl$ requires C, 65·6; H, 4·0%). The yield was 2 g. By adding ether to the filtrate a solid was precipitated which was extracted by boiling 0·5% hydrochloric acid; this gave a further 2·2 g. of chrysinidin chloride and left 5·5 g. of a dark red, insoluble material.

(D) A cold solution of *O*-benzoylphloroglucinaldehyde (1·6 g.) and acetophenone (3 g.) in dry ethyl acetate (30 c.c.) was saturated with hydrogen chloride and kept for 3 days. The orange-red liquid acquired a greenish-yellow fluorescence and gradually deposited crystals (2 g.). The orange *O*-benzoylchrysinidin chloride (1·9 g.) was dissolved in methyl alcohol (100 c.c.) and the solution was saturated with ammonia at 0° and kept at this temperature for 24 hours. The ammonia and methyl alcohol having been removed under diminished pressure at room temperature, the residue was dissolved in warm methyl alcohol (20 c.c.), and hot hydrochloric acid (40 c.c.) added. The amorphous precipitate was collected and extracted with boiling 0·5% hydrochloric acid, and the salt again precipitated from the filtered solution by the addition of concentrated hydrochloric acid. It was now partly crystalline and was converted into the perchlorate, which was fully purified.

Chrysinidin perchlorate. The various specimens of chrysinidin chloride have been identified with each other by conversion into this characteristic derivative, which crystallises from acetic acid in glistening, deep red, rectangular, prismatic needles (Found in material from B above: C, 53·3; H, 3·4. $C_{15}H_{11}O_7Cl$ requires C, 53·2; H, 3·3%). The substance darkens at 208° and melts with decomposition at 244°. It is very readily soluble in alcohol and on the addition of aqueous perchloric acid the substance crystallises in slender, glistening, orange-red needles. Careful comparison showed that all the specimens were identical; on the other hand, the chrysinidin obtained by demethylation of the dimethyl ether (Part VI, *loc. cit.*) must have been contaminated with methoxy-containing salts, since the perchlorate decomposed at 185°.

O-*Benzoylacacetinidin Chloride.*—A solution of *O*-benzoylphloroglucinaldehyde (0·6 g.) and *p*-methoxyacetophenone (2 g.) in dry ethyl acetate (30 c.c.) was saturated in the cold with hydrogen chloride; in the course of an hour it became deep orange and exhibited a striking greenish-yellow fluorescence. The mixture was kept for 3 days and the salt which had separated was then collected (2 g.); a further quantity (0·5 g.) was obtained by addition of ether to the filtrate. Concentrated hydrochloric acid was added to a solution of the salt in a hot mixture of equal volumes of alcohol and 0·5% hydrochloric acid until a faint turbidity appeared; on cooling, the substance crystallised in bright, orange-red sheaves of slender, prismatic needles (Found in material dried over sulphuric acid: C, 64·6; H, 4·7. $C_{23}H_{17}O_5Cl,H_2O$ requires C, 64·7; H, 4·5%). The alcoholic solutions of this benzoylacetinidin chloride are orange to orange-red and exhibit strong green fluorescence.

Acacetinidin Chloride (I).—The debenzoylation of benzoylacacetin-

idin chloride (3 g.) was accomplished in much the same way as described above in the case of benzoylchrysinidin chloride and the crude acacetinidin chloride (1·5 g.) was crystallised by solution in hot 0·5% hydrochloric acid and addition of concentrated hydrochloric acid until turbidity appeared. After three such processes, the salt was obtained in microscopic, reddish-brown balls. It was then crystallised by addition of concentrated hydrochloric acid to an alcoholic solution and obtained in prismatic needles, and on repetition in diamond-shaped and rhombic plates with a brilliant green reflex but exhibiting much twinning. A third crystallisation in this way gave clear-cut, individual crystals having a form identical with that of crystals of acacetinidin chloride (Part IV, *loc. cit.*). The reactions of the two specimens were also identical and in addition the perchlorates and picrates were examined and compared, with the result that no difference could be detected between the specimens of the respective derivatives obtained from benzoylacacetinidin chloride from acacetinidin chloride.

Acacetinidin perchlorate crystallised from hot aqueous perchloric acid in red, glistening, slender, prismatic needles and from acetic acid in red, elongated, pointed prisms having a bluish-green reflex. The substance darkens at 260° and melts at 278—280° (decomp.). A mixture of the two specimens behaved in the same way.

Acacetinidin picrate crystallised from 40% alcohol, containing picric acid, in long, red, prismatic needles which darkened at 220—225° and melted to a black liquid at 231—233° (mixed—the same).

Apigeninidin Chloride (5 : 7 : 4′-*Trihydroxyflavylium Chloride*).—Acacetinidin chloride (2·1 g.) was demethylated by gently boiling with hydriodic acid (60 c.c.; *d* 1·7) and phenol (9 g.) in a stream of carbon dioxide. Methyl iodide was rapidly evolved and after 15 minutes the acacetinidin iodide had passed into solution. The reaction was continued for a further 10 minutes; a test then proved that only traces of methyl iodide were being produced. On cooling, the apigeninidin iodide quickly crystallised in scarlet, prismatic needles and these were collected on asbestos, washed with ether, and dried at 100° (2·2 g.). The substance is readily soluble in hot alcohol and on the addition of hydrochloric acid the chloride crystallises from the solution, but in order to ensure complete conversion the following method was adopted. The iodide (2·2 g.) and silver chloride (about 10 g.) were added to ethyl alcohol (400 c.c.) and concentrated hydrochloric acid (5 c.c.), and the solution was boiled during 10 minutes, filtered and mixed with concentrated hydrochloric acid (50 c.c.). On cooling, apigeninidin chloride separated in very well-shaped, glistening, rhombic prisms. Individual crystals are seen under the microscope to be light orange-yellow by transmitted

light and the mass is bright salmon-red. The substance was washed with alcohol and dried in a vacuum (Found: C, 58·5; H, 4·4. $C_{15}H_{11}O_4Cl,H_2O$ requires C, 58·4; H, 4·2%). This hydrate is very stable and when quickly heated appears to suffer no change below 200°. At about 230° it darkens and turns green. The anhydrous substance chars above 350° but does not melt. Prolonged heating at 100° does not effect dehydration, but at 140° in a vacuum the substance loses weight and becomes hæmatite-red.

Apigeninidin chloride is sparingly soluble in hot dilute hydrochloric acid and in most organic solvents. On boiling with not too much water, it dissolves and at once separates again as a flocculent precipitate consisting of orange, microscopic needles. This substance is a basic chloride and on the addition of a drop of hydrochloric acid is converted into the normal salt, recognised by its characteristic mode of crystallisation in rhombic prisms. *n*-Butyl or *iso*amyl alcohol extracts most of the salt from aqueous solution, giving an orange-red solution, but the aqueous layer always retains a canary-yellow colour. This behaviour differs from that of pelargonidin chloride, which is completely extracted from aqueous solution by *iso*amyl alcohol. The bright yellow solution in concentrated sulphuric acid exhibits an intense green fluorescence. The colour base, obtained by the action of sodium acetate on the chloride in aqueous solution, is a brownish-red precipitate, sparingly soluble in butyl alcohol to an eosin-red solution. On great dilution, the yellow solutions of apigeninidin salts become red, but under no conditions is a colourless pseudo-base formed. The chloride or the colour base dissolves in aqueous sodium carbonate or ammonia to a rich crimson solution, the colour of which is much bluer, brighter and more persistent on dilution than that of an alkaline solution of acacetinidin chloride. The orange-red solution in alcohol becomes intense yellowish-brown on the addition of ferric chloride. The ferrichloride could not be obtained because it is more soluble than the chloride. For example, a suspension of the chloride in boiling acetic acid gives a clear solution on the addition of a little ferric chloride dissolved in concentrated hydrochloric acid, but on cooling the chloride separates. The *mercurichloride* is extremely sparingly soluble in dilute hydrochloric acid containing mercuric chloride and crystallises in hair-like, orange, microscopic needles. The chloride dissolves somewhat readily in hot dilute perchloric acid and on quickly cooling the *perchlorate* separates in very slender, long, irregular fibres which, on standing in contact with the solvent, change into very dense clusters of microscopic needles. The *periodide* behaves similarly, being precipitated as a stringy, dark brown mass which is resolved into slender needles. Numerous attempts to

oxidise apigeninidin to apigenin were fruitless. The alkaline solution retains its colour when air is aspirated through it during 12 hours.

Hydroxymethyleneacetoveratrone.—Methyl alcohol (1·6 g.) was added to a suspension of granular sodium (1·1 g.) in dry ether (50 c.c.) and when the formation of alkyloxide was complete a mixture of ethyl formate (5·2 g.) and acetoveratrone (9·7 g.) was slowly introduced with frequent shaking; a white, pasty mass was formed. Next day, ice, acetic acid, and ether were added and the separated ethereal solution was shaken with a concentrated solution of copper acetate. The *copper* derivative (7·0 g.) crystallised from toluene in pale green needles which softened at 180° and decomposed at 188° (Found: Cu, 13·0. $C_{22}H_{22}O_8Cu$ requires Cu, 13·3%). Similarly, the *copper* derivative of hydroxymethylene-2:4-dimethoxyacetophenone was obtained from resacetophenone dimethyl ether (yield, 13 g. from 14 g. of the ketone). It crystallised from toluene in pale green prisms, m. p. 190° (Found: Cu, 13·4%).

5:7-*Dihydroxy*-3':4'-*dimethoxyflavylium Chloride.*—An ethereal solution of hydroxymethyleneacetoveratrone (itself an oil exhibiting the usual properties of its class) was obtained by shaking the copper derivative (5·5 g.) with dilute sulphuric acid and ether; the separated ethereal layer was dried with sodium sulphate. This solution was added to one of anhydrous phloroglucinol (3 g.) in ether, and a stream of hydrogen chloride led through the mixture for 4 hours. After 12 hours, the bright red condensation product was collected, washed with ether, and dried (5 g.). This product was boiled under reflux with alcohol (1500 c.c.) and concentrated hydrochloric acid (12 c.c.) for an hour, and the solution distilled until separation of the salt commenced. After keeping for 24 hours, the solid was collected and further purification was effected by solution in and separation from 2% hydrochloric acid. After several such processes, the substance crystallised in a homogeneous form in opaque, microscopic, spherical masses. Further slow crystallisation from hot dilute solutions gave reddish-brown, prismatic needles which decomposed at 272° (Found in material dried in a vacuum over sulphuric acid: C, 56·4; H, 4·8. $C_{17}H_{15}O_5Cl,1·5H_2O$ requires C, 56·5; H, 4·9%). This salt dissolves in aqueous sodium carbonate to an intense blood-red solution.

Demethylation. A mixture of this luteolinidin dimethyl ether (1·4 g.) with phenol (4 g.) and concentrated hydriodic acid (30 c.c.) was boiled in an atmosphere of carbon dioxide for 30 minutes. A bright red iodide crystallised from the solution and this was collected and converted in the usual manner into the corresponding *chloride.* The latter crystallised from alcohol in small, orange-red needles,

which decomposed at 282° (Found in material dried in a vacuum over sulphuric acid: C, 58·6; H, 3·4; MeO, 10·5; Cl, 10·1; loss at 105° in a high vacuum, 2·7. $C_{16}H_{12}O_5Cl,0{\cdot}5H_2O$ requires C, 58·4; H, 3·7; 1MeO, 9·5; Cl, 10·7; H_2O, 2·8%). The substance is therefore a luteolinidin chloride monomethyl ether. It gives a Bordeaux-red to reddish-purple solution in aqueous sodium carbonate and its acid solutions have the same colour as those of luteolinidin chloride. The alkali colour reaction provides the only available evidence in regard to constitution and suggests that the salt is 5 : 7 : 4′-trihydroxy-3′-methoxyflavylium chloride rather than the possible isomeride. The purified substance must contain a trace of luteolinidin chloride, since it gives a weak ferric chloride reaction. On further demethylation with a mixture of hydriodic acid (*d* 1·75) and phenyl acetate, during the course of which the rate of evolution of methyl iodide was observed, luteolinidin iodide was obtained. The corresponding chloride showed all the reactions and properties of the substance previously obtained from luteolinidin chloride trimethyl ether (Part VI, *loc. cit.*).

7-*Hydroxy*-3 : 2′ : 4′-*trimethoxyflavylium Chloride*.—A solution of ω : 2 : 4-trimethoxyacetophenone (4·4 g.) and β-resorcylaldehyde (2·8 g.) in dry ether (100 c.c.) was saturated with hydrogen chloride for 2 hours and kept over-night. The product separated in orange-red needles with a dark green reflex (8 g.). It crystallised from dilute hydrochloric acid in crimson, prismatic needles which darkened at 140° and decomposed at 185° (Found in material dried in a vacuum over sulphuric acid: C, 58·8; H, 5·4. $C_{18}H_{17}O_5Cl$ requires C, 59·0; H, 5·2%). The colour base is bluish-red, a pseudo-base is readily formed, and the yellow solution in concentrated sulphuric acid exhibits bright apple-green fluorescence.

3 : 7 : 2′ : 4′-*Tetrahydroxyflavylium Chloride* (*Resomorinidin Chloride*) (II).—A mixture of the trimethyl ether (4 g.), phenol (8 g.), and hydriodic acid (80 c.c.; *d* 1·7) was gently boiled during 35 minutes in a stream of carbon dioxide. On cooling, glistening prismatic needles, exhibiting golden-green reflex, separated and these were collected and dried (2·8 g.). Conversion into chloride by means of silver chloride and a trace of hydrogen chloride was accomplished in alcoholic solution and, on the addition of 10% aqueous hydrochloric acid to the filtrate, the salt crystallised in small, red needles which decomposed at 216° (Found in material dried in a vacuum over sulphuric acid: C, 54·3; H, 4·2. $C_{15}H_{11}O_5Cl,1{\cdot}5H_2O$ requires C, 54·0; H, 4·2%). Resomorinidin chloride is very sparingly soluble in cold dilute hydrochloric acid and moderately easily soluble in the hot solvent to an orange-red solution. Its solution in sulphuric acid exhibits bright apple-green

fluorescence. Sodium carbonate added to an aqueous solution gives an intense reddish-violet or permanganate-like coloration. An alcoholic solution of the salt is bluish-red and on addition of sodium carbonate becomes dichroic, red in thick layers, blue in thin layers, and exhibits dark red fluorescence. A hydrochloric acid solution was decolorised on boiling with zinc dust, and the cooled mixture was then extracted with ether. Addition of very dilute sodium hydroxide to the separated ethereal layer gave a blue solution which soon became violet and then rose-coloured. On warming, the aqueous layer became greenish-yellow and developed an intense ivy-green fluorescence.

Ethyl 2 : 4 : 6-*Trimethoxybenzoylpyruvate*, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$. —This substance was prepared in the hope that it might prove to be a convenient source of 5 : 7-dimethoxychromone, which was required in connexion with attempts to obtain representatives of the *epi*flavylium series. Phloracetophenone trimethyl ether (5·2 g.) (Kostanecki and Tambor, *Ber.*, 1899, **32**, 2261) and ethyl oxalate (5·5 g.) were added to an absolute alcoholic solution (30 c.c.) of sodium ethoxide (1·4 g. of sodium) and next day ether was added to complete the separation of the sodium derivative. This was collected and dissolved in water and the *ester*, liberated by means of acetic acid, was isolated (5 g.); it crystallised from aqueous alcohol in long, pale yellow needles, m. p. 84° (Found: C, 58·3; H, 5·9. $C_{15}H_{18}O_7$ requires C, 58·1; H, 5·8%). This ester exhibits the usual properties of its class and in the solid state, preferably as a well dispersed precipitate suspended in a faintly acid medium, forms a highly characteristic blue compound with iodine.

The authors wish to thank the Royal Society and the Chemical Society for grants which have defrayed a part of the cost of the investigation.

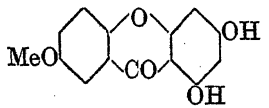
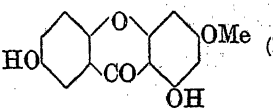
THE UNIVERSITY OF MANCHESTER. [*Received, June 21st*, 1927.]

CCLIX.—*The Constitution of Gentisin.*

By JUNZO SHINODA.

GENTISIN was first isolated from gentian root by Henry and Caventou (*J. Pharm. Chim.*, 1821, 178) and was subsequently examined by Baumert (*Annalen*, 1847, **62**, 106) and by Hlasiwetz and Habermann (*ibid.*, 1875, **175**, 63; 1876, **180**, 343). The investigations of Kostanecki and his co-workers have proved that gentisin is the monomethyl ether of gentisein, which is 1 : 3 : 7-

trihydroxyxanthone and was synthesised by Kostanecki and Tambor (*Monatsh.*, 1894, **15**, 1) by condensation of phloroglucinol and quinolcarboxylic acid. An attempt of these investigators to obtain 1 : 3-dihydroxy-7-methoxyxanthone along similar lines was unsuccessful (*Monatsh.*, 1895, **16**, 920). Kostanecki, however, showed that gentisein on methylation yields gentisin and that gentisin yields only a monomethyl ether. This excludes the possibility that gentisin is 3 : 7-dihydroxy-1-methoxyxanthone and this substance must therefore be 1 : 3-dihydroxy-7-methoxyxanthone (I) or 1 : 7-dihydroxy-3-methoxyxanthone (II).

(I.)  (II.) 

From the behaviour of bisazobenzene-gentisin, Perkin (J., 1898, **73**, 1028) has indicated that gentisin should be represented by the formula (II), and the present author now confirms this conclusion, since the compound (I) described in this communication is quite different from gentisin. The methyl group of gentisin is thus in a position similar to that which it occupies in rhamnetin and rhamnazin. The synthesis of (I) has been effected by an application of the Hoesch reaction following the similar preparation of 1 : 3-dihydroxyxanthone by Nishikawa and Robinson (J., 1922, **121**, 839).

EXPERIMENTAL.

2-*Hydroxy*-5-*methoxybenzaldoxime*, obtained in the usual manner from 2-hydroxy-5-methoxybenzaldehyde, crystallised from water in colourless, prismatic needles, m. p. 118° (Found: C, 57·4; H, 5·8. $C_8H_9O_3N$ requires C, 57·4; H, 5·4%). 2-*Hydroxy*-5-*methoxybenzonitrile*, obtained on treatment of the oxime with boiling acetic anhydride for 3 hours and subsequent hydrolysis with 10% sodium hydroxide solution, crystallised from water in colourless needles, m. p. 136° (Found: C, 64·0, 64·5; H, 5·0, 4·7. $C_8H_7O_2N$ requires C, 64·4; H, 4·7%).

1 : 3-*Dihydroxy*-7-*methoxyxanthonimine Hydrochloride*.—A mixture of 2-hydroxy-5-methoxybenzonitrile (5 g.), anhydrous phloroglucinol (4 g.), zinc chloride (5 g.), and dry ether (30 c.c.) was saturated with hydrogen chloride with frequent shaking. After a few hours, yellow crystals separated, but later these gave place to a deep yellow solution and then to orange crystals. After 10 days, water was added and the insoluble material (A) collected. The filtrate was extracted with ether and then concentrated; on cooling, yellow crystals (B) separated (Found: HCl, 12·1. $C_{14}H_{12}O_4NCl$ requires HCl, 12·4%). The properties of (A) and (B) are very similar; both

are very sparingly soluble in most organic solvents and dissolve in concentrated sulphuric acid to a yellow solution which exhibits green fluorescence. The solution in aqueous alkalis is yellow.

1 : 3-*Dihydroxy*-7-*methoxyxanthone* (I).—The ketimine hydrochloride was hydrolysed by means of boiling aqueous sodium hydroxide (until ammonia was no longer evolved) and the *isogentisin* was then precipitated by the addition of dilute sulphuric acid as a gelatinous mass that became crystalline when the liquid was boiled. The substance crystallised from aqueous alcohol in elongated, yellow plates, m. p. 241° (Found: C, 64·8; H, 4·3. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%).

The yellow solution in concentrated sulphuric acid exhibits green fluorescence, and ferric chloride added to an alcoholic solution develops a greenish-black coloration. The substance does not reduce an ammoniacal silver nitrate solution. A distinction from gentisin is that when an alkaline solution is agitated with sodium amalgam it becomes, like gentisein, blood-red; gentisin gives a deep green coloration under these conditions. On acetylation, a *derivative*, m. p. 211—212°, was obtained.

The *iso*gentisin was demethylated by means of boiling hydriodic acid; the gentisein obtained crystallised from methyl alcohol in orange-yellow needles, m. p. 318° with darkening from 310°. The substance had the properties attributed to it by Kostanecki and on acetylation gave the triacetyl derivative; this crystallised from acetic acid in white, silky needles which, alone or mixed with a specimen obtained by Kostanecki's method (*Monatsh.*, 1891, **12**, 205), melted at 226°.

PHARMACEUTICAL INSTITUTE, TOKUSHIMA TECHNICAL COLLEGE, JAPAN. [*Received, July 11th*, 1927.]

CCLX.—*Syntheses of Cyclic Compounds. Part I. Ethyl βγ-Dimethylbutane-aaδδ-tetracarboxylate and some* cyclo*Butane Compounds derived therefrom.*

By ISRAEL VOGEL.

IN extending his investigations on the reduction of unsaturated compounds by moist aluminium amalgam (this vol., p. 594), the author has been led to examine the reduction of esters of the type CR′R″:CX·CO_2Et (I), where X may be CO_2Et, COMe, or CN, and R′,R″ may be Me,H; Ph,H; Me,Me; or the *cyclo*pentane or *cyclo*hexane ring. Coupling would presumably take place in the β-positions (compare Vogel, *loc. cit.*), resulting in the formation of compounds

II) which (if X = CO_2Et) are homologues, symmetrically substituted in the β- and γ-positions, of ethyl butanetetracarboxylate, a

(II.) $\begin{matrix} CR'R''\cdot CHX\cdot CO_2Et \\ CR'R''\cdot CHX\cdot CO_2Et \end{matrix}$ $\begin{matrix} CHMe\cdot CH(CO_2Et)_2 \\ CHMe\cdot CH(CO_2Et)_2 \end{matrix}$ (III.)

substance which has found wide application as a synthetic agent in the hands of Professor Perkin and his collaborators (see numerous papers in J., 1884—1900). This series of researches has therefore been instituted with the following objects: (1) to synthesise compounds of the type (II); (2) to study the influence of groups and rings in the β- and γ-positions on (*a*) the relative ease of formation and stability of four-, five-, six-, and higher-membered rings by condensation with the appropriate reagents, and (*b*) the stability of the *cis*- and *trans*-anhydrides of the cyclic dibasic acids; (3) to synthesise substituted adipic acids from compounds of the type (II) and to employ them in the investigation of the stability of the *cis*- and *trans*-anhydrides as well as of their simpler cyclic derivatives.

The present communication is concerned with the reduction of ethyl ethylidenemalonate by moist aluminium amalgam.* This substance has been previously reduced by means of moist sodium amalgam by Higginbotham and Lapworth (J., 1923, **123**, 1618), who state that "products of at least two distinct types," a volatile β-ketonic ester and a bimolecular compound (III), are formed. No conclusive evidence as to the presence of the β-ketonic ester was given, nor was the dimethylbutanetetracarboxylate isolated, its presence in the primary reduction product being inferred from the production of two isomeric ββ′-dimethyladipic acids by hydrolysis, heating at 160°, and subsequent distillation under low pressure. The author, by employing moist aluminium amalgam as the reducing agent, has found no difficulty in preparing *ethyl dimethylbutanetetracarboxylate* (III) in quantity. On hydrolysis with alcoholic potassium hydroxide, it readily yields a mixture of two stereoisomeric *βγ-dimethylbutane-ααδδ-tetracarboxylic acids*, which can be separated into two forms (*meso* and racemic) melting at 152—154° (decomp.) and 185—185·5° (decomp.), respectively. The racemic configuration is provisionally assigned to the less fusible form. On heating the mixture of the two tetracarboxylic acids at 200°, carbon dioxide was eliminated and a mixture of the two corresponding ββ′-dimethyladipic acids was obtained melting over the range 105—120°, which on esterification and hydrolysis

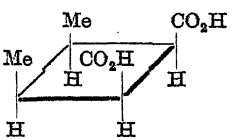
* A description of the application of moist aluminium amalgam in the separation of mixtures of unsaturated compounds, especially those exhibiting three-carbon tautomerism, is reserved for a future communication.

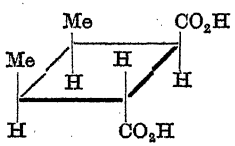
yielded chiefly a mixture of acids, m. p. 113—117° (compare Higginbotham and Lapworth, *loc. cit.*, who found the upper limit of m. p. range was 75° or 128°, according as acetic acid or sodium bicarbonate was used to minimise alkalinity in the sodium amalgam reduction). The description of the separation of the two isomeric ββ′-dimethyladipic acids as well as that of some of their derivatives is reserved for a future paper.

The use of ethyl dimethylbutanetetracarboxylate (III) in synthetical work depends on the fact that it readily yields a *disodium* compound (IV) on treatment with sodium ethoxide or preferably

(IV.) $\begin{matrix}\mathrm{CHMe{\cdot}CNa(CO_2Et)_2}\\ \mathrm{CHMe{\cdot}CNa(CO_2Et)_2}\end{matrix}$ $\begin{matrix}\mathrm{CHMe—C(CO_2Et)_2}\\ \mathrm{CHMe—C(CO_2Et)_2}\end{matrix}$ (V.)

sodium methoxide, the latter being very much more reactive than the former. By bromine, (IV) is quantitatively converted into *ethyl* 2 : 3-*dimethylcyclobutane*-1 : 1 : 4 : 4-*tetracarboxylate* (V). The latter on hydrolysis with alcoholic potash yields the corresponding tetracarboxylic acid, which, on heating to 180°, esterification, and subsequent hydrolysis with alcoholic potassium hydroxide, gives rise to a mixture of the two cyclo*butanedicarboxylic acids* (VI) and (VII), melting respectively at 87—88° and 200·5—201·5°. They

(VI.) 



(VII.)

may be separated by treatment with acetyl chloride (compare Auwers and Thorpe, *Ber.*, 1895, **28**, 623; Komppa, *Annalen*, 1909, **368**, 152; 1909, **370**, 209; Perkin and Scarborough, J., 1921, **119**, 1405); the *trans*-acid remains unaffected whilst the *cis*-acid is converted into the anhydride.

Further evidence in support of ring closure is provided by comparison of the physical properties of the esters (Table I).

TABLE I.

Substance.	B. p.	*d*.	*n*.	$[R_L]$ obs.	$[R_L]$ calc.
$\begin{matrix}\mathrm{MeCH{\cdot}CH(CO_2Et)_2}\\ \mathrm{MeCH{\cdot}CH(CO_2Et)_2}\end{matrix}$	225—226°/16 mm.	1·0887	1·44873	92·16	91·93
$\begin{matrix}\mathrm{MeCH—C(CO_2Et)_2}\\ \mathrm{MeCH—C(CO_2Et)_2}\end{matrix}$ *	208—210°/16 mm.	1·1216	1·45573	90·16	89·73
$\begin{matrix}\mathrm{MeCH{\cdot}CH_2{\cdot}CO_2Et}\\ \mathrm{MeCH{\cdot}CH_2{\cdot}CO_2Et}\end{matrix}$	139—141°/15 mm.	0·98777	1·43447	60·74	60·92
$\begin{matrix}\mathrm{MeCH—CH{\cdot}CO_2Et}\\ \mathrm{MeCH—CH{\cdot}CO_2Et}\end{matrix}$	138—139°/14 mm.	1·00955	1·43888	59·43	58·72

* Slightly impure. See p. 1991.

No details as to temperature, etc., are included, as they are given in full in the experimental section. It is evident that whilst there is no great difference in the boiling points, there are marked differences in the densities and the refractivities, those of the cyclic being greater than those of the corresponding open-chain compounds. The exaltations of the molecular refractivity for the D line of the two *cyclo*butane compounds (0·43 and 0·71) are comparable with those previously observed by other workers for the *cyclo*butane ring (compare Oestling, J., 1912, **101**, 457, mean value 0·48; Eisenlohr, "Spektrochemie organische Verbindungen," 1912, mean value 0·46; Lebedev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1388, mean value 0·60; Zelinsky, *Ber.*, 1913, **46**, 1093; 1927, **60**, 711, mean value 0·45; Kon, J., 1922, **121**, 513, from *cyclo*hexane*spirocyclo*butanone, 0·77).

The analogous unsubstituted open-chain and *cyclo*butane compounds were prepared many years ago by Perkin (J., 1887, **51**, 1; 1894, **65**, 572). Whilst speculations as to the effect of groups are at present premature—it is hoped to discuss the question fully when a larger number of substituted derivatives have been studied—it may be added that the properties of the $\beta\gamma$-dimethyl homologues are very similar to those of the corresponding unsubstituted compounds, a result which would be expected from the modified strain theory of Thorpe and Ingold, since the normal tetrahedral angle of 115·3° has been altered only to 112·5° (compare Ingold, Sako, and Thorpe, J., 1922, **121**, 1177; Ingold, *ibid.*, p. 2676) by the substitution of CHMe for CH_2. It is a curious fact that the only *cyclo*butanedicarboxylic acid directly isolated by Perkin (*loc. cit.*) was the *cis*-acid, the *trans*-acid being prepared by heating the *cis*-acid with hydrochloric acid at 190°, whereas in the case of the corresponding *cyclo*pentanedicarboxylic acids the *trans*-acid was the only form directly isolated. In the present research, both forms were directly isolated.

The question of the existence of two anhydrides of a *cyclo*butane-1 : 2-dicarboxylic acid is of great interest. Baeyer (*Annalen*, 1890, **258**, 145) predicted from his strain theory that *trans*-anhydride formation should not take place in the *cyclo*propane and should occur in the *cyclo*pentane series, but he was doubtful whether it would be possible in the corresponding 1 : 2-*cyclo*butane-compounds. Perkin (J., 1894, **65**, 572), in testing this prediction experimentally for the unsubstituted *cyclo*butanedicarboxylic acids, found that the *trans*-acid was practically unaffected by heating with acetyl chloride, but on heating with acetic anhydride it was converted into the *cis*-anhydride. The author has found that *trans*-dimethyl-*cyclo*butane-1 : 2-dicarboxylic acid behaves similarly; on heating

it with acetic anhydride for 2 hours, the *cis*-anhydride is produced. It appears that the strain in the *trans*-anhydride is so great that the compound is incapable of isolation under the experimental conditions employed (compare Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 91, who have isolated the *trans*-anhydride of hexahydrohomophthalic acid and find that an equilibrium mixture of the *cis*- and *trans*-anhydrides is formed on heating it with acetic anhydride). The question whether the *cis*-anhydride is formed *via* the *cis*-acid or the *trans*-anhydride must still be regarded as an open one.

The ethyl dimethylbutanetetracarboxylate used in this research was obtained by the reduction of ethyl ethylidenemalonate (Goss, Ingold, and Thorpe, J., 1923, **123**, 3353) by moist aluminium amalgam; the yield averaged 45%, the remainder of the product consisting of unchanged malonic ester, which was readily separated by fractional distillation in a vacuum. This yield is surprising, since, under the conditions employed, reduction takes place quantitatively (mesityl oxide, benzylideneacetone) or not at all (ethyl ββ-dimethylacrylate). Two explanations are possible: (*a*) ethyl ethylidenemalonate decomposes under the influence of the moist aluminium amalgam, and (*b*) the ethylidenemalonate contains a considerable quantity of malonic ester which cannot be removed by fractionation in a vacuum. The latter explanation is probably the correct one and receives support from the analytical results as well as from a comparison of the molecular refractivities of Goss, Ingold, and Thorpe's ethyl ethylidenemalonate and that prepared directly from the acid, only the latter exhibiting the expected exaltation due to the presence of conjugated double bonds.

EXPERIMENTAL.

The yield of ethyl ethylidenemalonate, b. p. 113—135°/20 mm., prepared by Goss, Ingold, and Thorpe's method averaged 85 g. from 100 g. of malonic ester [Found: C, 54·5; H, 7·5. Calc. for $CH_3{\cdot}CH{:}C(CO_2Et)_2$: C, 58·1; H, 7·5%. Calc. for $CH_2(CO_2Et)_2$: C, 52·5; H, 7·5%]. On redistillation in a vacuum, a fraction was obtained having b. p. 111—112°/12 mm., $d_4^{17\cdot2°}$ 1·05237, $n_D^{17\cdot2}$ 1·42567, $[R_L]_D$ 45·29.

Ethylidenemalonic acid was obtained by adding 50 g. of acetaldehyde to 75 g. of malonic acid in 100 g. of pyridine at −5°, followed by 2·5 c.c. of piperidine during 1 hour, the whole being vigorously stirred. The reaction mixture was kept at 0° overnight, the orange-coloured solid mass cooled to −5° and decomposed with a slight excess of ice-cold dilute sulphuric acid, and the pale yellow ethylidenemalonic acid, m. p. 82° (Komnenos, *Annalen*,

1883, **218**, 165, gives m. p. 84), *quickly* separated. The acid, on esterification with absolute ethyl alcohol and sulphuric acid, yielded ethyl ethylidenemalonate, which was obtained pure after two fractionations in a vacuum. It had b. p. 115—117°/15 mm., $d_4^{17\cdot4°}$ 1·01938, $n_D^{17\cdot4°}$ 1·43007, $[R_L]_D$ 47·17 (calc., 46·60) (compare Komnenos, *loc. cit.*; $d^{15°}$ 1·0435) (Found: C, 57·8; H, 7·6. Calc. for $C_9H_{14}O_4$: C, 58·1; H, 7·5%).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl βγ*-Dimethylbutane-*αα*δδ-tetracarboxylate* (III).—Ethyl ethylidenemalonate (b. p. 113—135°/20 mm.; 150 g.) was reduced by 200 g. of aluminium amalgam prepared by the author's method (this vol., p. 594). The product was worked up in the usual manner and fractionated in a vacuum. Ethyl malonate was recovered below 140°/16 mm.; the temperature then rose rapidly to 210° and *ethyl* βγ*-dimethylbutane-*αα*δδ-tetracarboxylate* distilled at 210—240°/16 mm. (yield, 68 g. or 45%). On refractionation, the pure ester was obtained; it had b. p. 225—226°/16 mm., $d_4^{17·0°}$ 1·0887, $n_D^{17·0°}$ 1·44873, $[R_L]_D$ 92·16 (calc., 91·93) (Found: C, 57·6; H, 8·0. $C_{18}H_{30}O_8$ requires C, 57·8; H, 8·0%). It is a viscid, colourless liquid having a faint odour and on exposure to the atmosphere it slowly becomes pale yellow. The *disodio*-compound (IV) is best prepared from the pure ester and anhydrous sodium methoxide (see below). After being washed with a mixture of pure dry ethyl alcohol and pure dry ether (1 : 3), it is obtained as a pale yellow solid (Found: Na, 11·0. $C_{18}H_{28}O_8Na_2$ requires Na, 11·0%). It decomposes on exposure to the atmosphere.

Hydrolysis of the ester (III). Solutions of the ester (30 g.) in ethyl alcohol (60 g.) and of potassium hydroxide (30 g.) in water (60 g.) were mixed, heated on the steam-bath for 6 hours, and evaporated to dryness. The residue was dissolved in a little water, the solution was extracted with ether to remove any unchanged ester if present and acidified with dilute sulphuric acid, the small quantity of resinous matter which separated was removed by filtration, and the pale yellowish-brown filtrate was saturated with ammonium sulphate and extracted seven times with ether. After *slow* evaporation of the ether, a yellow oil remained which immediately solidified to an almost colourless, crystalline solid (yield, 16 g.), m. p. 155—162° (decomp.). On addition of pure dry ether, the major portion dissolved and a crystalline solid, m. p. 177—179° (decomp.), remained. This was almost pure r-βγ*-dimethylbutane-*αα*δδ-tetracarboxylic acid* (Found: C, 45·6; H, 5·5; equiv., by titration, 66. $C_{10}H_{14}O_8$ requires C, 45·8; H, 5·3%; equiv., 65·5).

Separation of the Two βγ*-Dimethylbutane-*αα*δδ-tetracarboxylic Acids.*—The *r*-acid could be readily isolated from the mixture,

m. p. 155—162° (decomp.) (Found: C, 45·5; H, 5·5%; equiv., by titration, 66), by fractional crystallisation from concentrated hydrochloric acid, in which it was only moderately easily soluble. It was thus obtained in small, hard prisms, m. p. 185—185·5° (decomp.) (Found: C, 45·7; H, 5·4%; equiv., by titration, 66). Other solvents which may be used for the separation are acetone, benzene–alcohol, and ethyl acetate. The *meso*-acid, which is much more soluble than the *r*-acid, can be isolated from the mother-liquors and has m. p. 152—154° (decomp.).

Conversion into a Mixture of ββ′-Dimethyladipic Acids.—Ten g. of the mixture of the tetracarboxylic acids were gradually heated to 200°; the evolution of carbon dioxide then ceased. The whole solidified on cooling to a yellowish-brown mixture (6 g.), m. p. 105—120°, of the two stereoisomeric ββ′-dimethyladipic acids (compare Higginbotham and Lapworth, *loc. cit.*). On esterification with absolute ethyl alcohol and sulphuric acid, the mixed esters, *ethyl ββ′-dimethyladipate*, were obtained. After two fractionations in a vacuum, the liquid had b. p. 139—141°/15 mm., $d_4^{19\cdot5°}$ 0·98777, $n_D^{19\cdot5°}$ 1·43447, $[R_L]_D$ 60·74 (calc., 60·92) (Found: C, 62·4; H, 9·7. $C_{12}H_{22}O_4$ requires C, 62·6; H, 9·6%). It was a mobile liquid with a pleasant ethereal odour. The mixture of esters on hydrolysis with alcoholic potassium hydroxide yielded chiefly a crystalline solid, m. p. 113—117° (Found: equiv., by titration, 89. $C_8H_{14}O_4$ requires equiv., 87).

Synthesis of the cyclo*Butane Ring. Formation of Ethyl* 2 : 3-*Dimethyl*cyclo*butane*-1 : 1 : 4 : 4-*tetracarboxylate* (V).—To 5·3 g. of "molecular" sodium under 200 c.c. of pure dry ether, 15·0 c.c. of pure dry ethyl alcohol were added. When all the sodium had reacted (gentle warming was necessary), a solution of the pure ester (III) (40 g.) in pure dry ether (160 c.c.) was carefully added; the disodio-compound (IV) gradually separated. The mixture was stirred mechanically and dry bromine (5·7 g.) added during 1 hour. The stirring was continued for a further hour, and water then added to dissolve the precipitated sodium bromide. The solution was washed with dilute aqueous sodium bicarbonate and with water and dried with anhydrous sodium sulphate. On evaporation of the ether, a viscid reddish-brown oil (39 g.) was obtained: this was used in all the experiments described below. On fractionation in a vacuum, some carbonisation occurred (compare the corresponding open-chain ester, which distilled unchanged), but most of the liquid distilled as a colourless oil, b. p. 208—210°/16 mm.; this, however, darkened somewhat on exposure to the atmosphere. It had $d_4^{16\cdot7°}$ 1·1216, $n_D^{16\cdot7°}$ 1·45573, $[R_L]_D$ 90·16 (calc., 89·73). Owing probably to the presence of a trace of bromine in the ester, the

analytical results were unsatisfactory (Found: C, 56·4; H, 7·7. $C_{18}H_{28}O_8$ requires C, 58·1; H, 7·5%) (compare Perkin and Robinson, J., 1921, **119**, 1397, who obtained unsatisfactory analytical results for ethyl *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylate).

It was subsequently found that a much more convenient method of preparation was to use anhydrous sodium methoxide, prepared from "molecular" sodium and pure dry methyl alcohol; the separation of the disodio-compound was then practically complete after 1 hour. The procedure was as described above, the quantities being 6·5 g. of sodium, 11·3 c.c. of methyl alcohol, 250 c.c. of ether; 50 g. of ester in 200 c.c. of ether; and 13·5 c.c. of bromine. The yield of crude *cyclo*butane ester was 49 g. It is not advisable to work with larger quantities, as the yield is thereby materially diminished.

Hydrolysis of the ester (V). Solutions of the ester (50 g.) in alcohol (100 g.) and of potassium hydroxide (50 g.) in water (100 g.) were used. The procedure was that described for the hydrolysis of the ester (III) (p. 1990). The dried ethereal extracts yielded 23 g. of a thick, pale yellow oil—this was employed in all the experiments described below. It slowly crystallised in a vacuum desiccator over concentrated sulphuric acid. The acid separated from ether–light petroleum (b. p. 40—60°) in star-shaped clusters or from benzene–light petroleum in needles, m. p. 138—139° (slight softening at 80°). Correct analytical results for the tetrabasic acid could not be obtained (compare Simonsen, J., 1908, **93**, 1785, who could not obtain correct analytical results for δ-methoxybutane-αα*γγ*-tetracarboxylic acid).

Preparation of a Mixture of the cis- *and* trans-*Forms of* 2 : 3-*Dimethyl*cyclo*butane*-1 : 4-*dicarboxylic Acid*, (VI) *and* (VII).—The tetracarboxylic acid (V) (20 g.) was heated gradually to 180°; the evolution of carbon dioxide then ceased. The gummy residue (compare the ββ′-dimethyladipic acids, which gave a crystalline solid) was esterified with absolute ethyl alcohol and sulphuric acid, and after two fractionations in a vacuum the mixed esters (9·5 g.), *ethyl* 2 : 3-*dimethyl*cyclo*butane*-1 : 4-*dicarboxylate*, were obtained as a fairly mobile liquid with a pleasant ethereal odour and having b. p. 138—139°/14 mm., $d_4^{16\cdot8°}$ 1·00955, $n_D^{16\cdot8°}$ 1·43888, $[R_L]_D$ 59·43 (calc., 58·72) (Found: C, 63·5; H, 8·6. $C_{12}H_{20}O_4$ requires C, 63·2; H, 8·8%). The ester (10 g. in 20 g. of ethyl alcohol) was refluxed with potassium hydroxide (10 g. in 20 g. of water) on the steam-bath for 5 hours. The solution was then evaporated to dryness, the almost colourless residue dissolved in a little water, and the solution extracted with ether, carefully acidified with dilute sulphuric acid, and extracted seven times with ether. The ethereal solution, after being dried with anhydrous sodium sulphate and

evaporated, yielded a colourless oil which immediately crystallised on agitation. On treatment with small quantities of pure dry ether, all the *cis*- and some *trans*-acid dissolved, leaving pure trans-2 : 3-*dimethylcyclobutane*-1 : 4-*dicarboxylic acid*, m. p. 200—201·5°, as a crystalline solid (Found: C, 55·7; H, 7·1; equiv., by titration, 85. $C_8H_{12}O_4$ requires C, 55·9; H, 7·0%; equiv., 86). On evaporation of the ether, a mixture of the *cis*- and *trans*-acids was obtained.

Separation of the cis- *and* trans-*Forms of* 2 : 3-*Dimethylcyclobutane*-1 : 4-*dicarboxylic Acid.*—The mixed acids (2 g.) were warmed to 50° with 4 g. of pure acetyl chloride; a vigorous reaction ensued and hydrogen chloride was evolved. After 1 hour, the liquid mass, containing some suspended crystalline solid (*trans*-acid), was placed in a vacuum desiccator over caustic potash; the excess acetyl chloride was almost wholly removed after 2 days. The semi-solid mass was treated with pure dry ether; some *trans*-acid remained undissolved which, after being washed with small quantities of ether, melted at 200·5—201·5°; the m. p. was unaffected by recrystallisation from acetone–petroleum (b. p. 40—60°). The ethereal solution was washed with dilute aqueous sodium carbonate then with water, and dried with anhydrous sodium sulphate, and the ethereal solution was allowed to evaporate spontaneously. The cis-*anhydride* of 2 : 3-*dimethylcyclobutane*-1 : 4-*dicarboxylic acid* separated in needles, m. p. 50—51° (Found: C, 62·0; H, 6·5. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%). On acidifying the sodium carbonate washings and repeatedly extracting them with ether, more *trans*-acid was obtained. An aqueous solution of the *cis*-anhydride, on being allowed to concentrate over sulphuric acid, yielded the crystalline cis-*acid*, m. p. 87—88° (Found: C, 55·8; H, 7·0; equiv., by titration, 87. $C_8H_{12}O_4$ requires C, 55·9; H, 7·0%; equiv., 86).

By distilling the mixed acids in a vacuum, the *cis*-acid together with some anhydride, which passes over at a slightly lower temperature, is obtained; this provides the simplest method for the preparation of the pure *cis*-acid or of the *cis*-anhydride.

Attempt to Prepare the Anhydride of trans-2 : 3-*Dimethylcyclobutane*-1 : 4-*dicarboxylic Acid.*—The pure *trans*-acid (1 g.) was gently boiled with an excess of pure redistilled acetic anhydride for 2 hours, and the excess of acetic anhydride removed over caustic potash in a vacuum desiccator. An ethereal solution of the oily residue was washed with dilute aqueous sodium carbonate and with water, dried with anhydrous sodium sulphate, and allowed to evaporate. The *cis*-anhydride, m. p. 50—51°, either alone or when mixed with a specimen prepared from the *cis*-acid, separated in needles.

In conclusion, I wish to thank Professor J. F. Thorpe, F.R.S., for his kind interest and advice. Some of the expenses of the research were met by a grant from the Chemical Society Research Fund.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, May 14th*, 1927.]

CCLXI.—*Chlorocamphoranilic Acids and Camphorochlorophenylimides.*

By MAHAN SINGH and RAM SINGH.

IN a previous communication (J., 1925, **127**, 1966) it was shown that the reaction

$$C_8H_{14}\begin{matrix}CO\cdot NH\cdot C_6H_4R\\ CO\cdot OH\end{matrix} \longrightarrow C_8H_{14}\begin{matrix}CO\\ CO\end{matrix}N\cdot C_6H_4R + H_2O$$

is dependent on the nature of the group R and other factors, the stability of the acid increasing as R becomes more negative. The carboxycamphoranilic acids (*loc. cit.*) produced by the condensation of camphoric anhydride with aminobenzoic acids are very stable and have not been converted into camphorimides.

The reactions of camphoric anhydride with *o*-, *m*-, and *p*-chloroanilines have now been investigated. The object was to examine the effect of decrease in the negativity of R(CO_2H to Cl) on the above reaction. As expected, the condensation products yielded a mixture of chlorocamphoranilic acids and camphorimide derivatives, thus showing that with the decrease in the negativity of the group there is a tendency towards the formation of ring compounds. The position of the substituent seems to have some effect on the yield of the camphorimide, which is about 20% in the case of the para-derivative and 5 to 6% in the case of the ortho- and meta-derivative. This question is being fully investigated in the condensation products of camphoric anhydride and bromoanilines and iodoanilines.

Wootton (J., 1910, **97**, 405) also has condensed camphoric anhydride with chloroanilines. The melting points of his acids are lower than ours, because they contain the corresponding camphorimides formed in the condensations.

With regard to the optical rotations of the chlorocamphoranilic acids, (*a*) the *o*-chloro-acid gives negative values in acetone and methyl ethyl ketone and positive values in methyl alcohol and ethyl alcohol; (*b*) the relation between the molecular rotation and the position of the chlorine atom is in all solvents $p>m>o$; (*c*) the

molecular rotatory powers of these acids do not follow the order of the dielectric constants of the solvents used.

The following table gives the molecular rotatory powers of camphoranilic acid and some of its ortho-derivatives in methyl alcohol, ethyl alcohol, and acetone.

	$[M]_D$.		
	Methyl alcohol.	Ethyl alcohol.	Acetone.
H*	+150°	+131°	+101°
CO_2H	−584	−574	−551
CH_3*	+146	+144	+ 98
Cl	+ 57·8	+ 35·6	− 40·3

* Singh and Puri, J., 1926, 504.

The relative changes of rotatory power in methyl alcohol and acetone are given by $CO_2H > H > CH_3 > Cl$. This corresponds with the relative polarity of the groups as deduced from molecular inductive capacities (Rule, J., 1926, 553).

The molecular rotations of the *p*- and *m*-substituted camphorophenylimides are considerably lower than those of the corresponding acids, whereas in the case of the *o*-substituted derivatives they are of the same magnitude.

Experimental.

Condensation of Camphoric Anhydride with o-*Chloroaniline.*—Equimolecular quantities of these and a little fused sodium acetate were heated together at 145—150° for 4 hours. The product was dissolved in 90% alcohol, decolorised with animal charcoal, precipitated, and extracted with a dilute solution of sodium bicarbonate, which left a very small residue of camphoro-*o*-chlorophenylimide. This crystallised from alcohol in fine, light needles, m. p. 128° (Wootton, *loc. cit.*, gives m. p. 125—126°). It was soluble in acetone, methyl alcohol, and ether, but sparingly soluble in ethyl alcohol (Found: C, 65·6; H, 6·4; Cl, 12·2. Calc., for $C_{16}H_{18}O_2NCl$: C, 65·8; H, 6·2; Cl, 12·1%).

The bicarbonate solution was acidified and the amorphous solid obtained was recrystallised twice from 60% alcohol; it then melted at 165° (Wootton, *loc. cit.*, gives m. p. 139—140°, which is that of a mixture of 2′-chlorocamphoranilic acid and the imide). *2′-Chlorocamphoranilic acid* is soluble in acetone, methyl alcohol, and ethyl alcohol and moderately easily soluble in ether (Found: C, 62·2; H, 6·8; Cl, 11·2; equiv. by titration with NaOH, 311. $C_{16}H_{20}O_3NCl$ requires C, 62·0; H, 6·5; Cl, 11·5%; equiv., 309·5).

Condensation of Camphoric Anhydride with m-*Chloroaniline.*—The procedure was that described above. The alcoholic solution slowly deposited fine, silky needles of camphoro-*m*-chlorophenyl-

imide, which melted at 176° after recrystallisation (Wootton gives m. p. 172—173°). It was soluble in acetone, methyl alcohol, and ether, and sparingly soluble in ethyl alcohol (Found: C, 66·0; H, 6·9; Cl, 12·2%).

The alcoholic filtrate, on being concentrated, gave a further crop of impure imide. The filtrate from this was poured into a large volume of water, and the precipitate of 3′-chlorocamphoranilic acid thus obtained was dissolved in dilute sodium bicarbonate solution, reprecipitated, and crystallised from 60% alcohol, the pure acid separating in thin plates, m. p. 216—217° (Wootton gives m. p. 207—209°). It was soluble in acetone, methyl alcohol, and ethyl alcohol, and very sparingly soluble in ether (Found: C, 61·8; H, 6·85; Cl, 11·9%, equiv., 304).

Condensation of Camphoric Anhydride with p-*Chloroaniline.*—The procedure was that described above, and the solvent absolute alcohol. The solution slowly deposited stout, prismatic needles of camphoro-*p*-chlorophenylimide, which were twice recrystallised from alcohol; they then melted at 165° (Wootton gives m. p. 162—163°). The imide is soluble in acetone, methyl alcohol and ether, and very sparingly soluble in ethyl alcohol (Found: C, 65·5; H, 6·5; Cl, 12·3%).

From the united filtrates a second crop of the imide was obtained, m. p. 164—165°, after recrystallisation from alcohol. 4′-Chlorocamphoranilic acid, isolated in the same way as the *m*-compound, crystallised from alcohol in needles, m. p. 197° (Wootton gives m. p. 192—194°). It was soluble in acetone, methyl alcohol and ethyl alcohol, and sparingly soluble in ether (Found: C, 61·7; H, 6·6; Cl, 11·9%; equiv., 314).

In all the condensations, complete separation of the acid from the imide could be effected by fractional crystallisation from ethyl alcohol, but it was a rather tedious process.

Molecular rotations of the chlorocamphoranilic acids and camphorochlorophenylimides.

Solvent.	Conc. (g./25 c.c.).	Temp.	α_D.	$[\alpha]_D$.	$[M]_D$.
	2′-Chlorocamphoranilic acid.				
MeOH	0·4391	18°	+0·61°	+18·7°	+57·8°
EtOH	0·4444	,,	+0·41	+11·5	+35·6
Me_2CO	0·2654	,,	−0·28	−13·2	−40·8
MeEtCO	0·4210	,,	−0·29	− 8·6	−26·6
	3′-Chlorocamphoranilic acid.				
MeOH	0·1475	18	+0·62	+52·5	+162·4
EtOH	0·1384	,,	0·48	43·3	134·0
Me_2CO	0·1268	,,	0·32	31·5	97·5
MeEtCO	0·1306	,,	0·42	40·2	124·4

Solvent.	Conc. (g./25 c.c.).	Temp.	α_D.	$[\alpha_D]$.	$[M]_D$.
	4′-Chlorocamphoranilic acid.				
MeOH	0·1870	18°	+0·88	+58·8	+183·0
EtOH	0·1314	,,	0·54	51·3	158·7
Me_2CO	0·1493	,,	0·46	38·5	119·0
MeEtCO	0·1302	,,	0·51	48·9	150·3
	Camphoro-*o*-chlorophenylimide.				
MeOH	0·1522	25°	+0·16	+13·14	+38·3
EtOH	0·1592	,,	0·18	14·1	41·1
Me_2CO	0·2468	,,	0·24	12·1	35·2
MeEtCO	0·2348	,,	0·26	13·8	40·2
	Camphoro-*m*-chlorophenylimide.				
MeOH	0·2030	25°	+0·23	+14·16	+41·1
EtOH	0·2256	,,	0·25	13·8	40·2
	Camphoro-*p*-chlorophenylimide.				
MeOH	0·2014	25°	+0·32	+19·8	+51·7
EtOH	0·2589	,,	0·33	15·9	46·4
Me_2CO	0·2432	,,	0·28	14·3	41·7
MeEtCO	0·3326	,,	0·44	16·5	48·0

The readings were taken in a 2-dm. tube within ½ hour of making up the solution. There was no mutarotation.

We desire to thank Dr. H. B. Dunnicliff for his kindly interest in this work.

GOVERNMENT COLLEGE, LAHORE,
PUNJAB, INDIA. [*Received, May 30th,* 1927.]

CCLXII.—δ-d-*Bornylsemicarbazide and* δ-d-neo*Bornylsemicarbazide.*

By JOHN AUGUSTUS GOODSON.

FOR an investigation, which has so far given negative results, the author has had occasion to prepare a quantity of δ-*d*-bornylsemicarbazide and δ-*d*-*neo*bornylsemicarbazide. The use of such optically active semicarbazides for the resolution of racemic carbonyl compounds has been suggested by various workers and a number of them have been prepared, *e.g.*, camphoryl-ψ-semicarbazide (Forster and Fierz, J., 1905, **87**, 722), δ-α-phenylethylsemicarbazide (Wilson, Hopper, and Crawford, J., 1922, **121**, 866), and δ-menthylsemicarbazide (Wilson and Crawford, J., 1925, **127**, 103), whilst Forster and Attwell attempted to prepare β-bornylsemicarbazide (J., 1904, **85**, 1188), but in no case have these substances so far been used successfully for this purpose. δ-*d*-Bornylsemicarbazide

and δ-*d*-*neo*bornylsemicarbazide were only tried on one racemic ketone, *viz.*, 3-methyl*cyclo*hexanone, and although well-crystallised products were obtained, they did not separate into optical antipodes on fractional crystallisation from two solvents.

EXPERIMENTAL.

Acetone-δ-d-*bornylsemicarbazone*.—To *d*-bornylamine (10 g.) melted by immersion in an oil-bath at 175°, was added acetone-semicarbazone (7·5 g.) a little at a time, and the heating continued for 15 minutes. The cold crystalline product was recrystallised from alcohol, and active *acetone*-δ-d-*bornylsemicarbazone* obtained in anhydrous needles (yield, 76%), m. p. 141—148° (corr.), $[\alpha]_D^{20°}$ + 25·5° (c = 2·04 in dry alcohol) (Found : C, 66·7; H, 10·0; N, 16·5. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 10·0; N, 16·7%).

In order to obtain a good yield, it is necessary to use anhydrous *d*-bornylamine. In a preliminary experiment, *d*-bornylamine containing two molecules of water of crystallisation, obtained by precipitation with sodium hydroxide from a solution of the hydrochloride, was used; a considerable quantity of di-*d*-bornylcarbamide was then produced.

δ-d-*Bornylsemicarbazide Hydrochloride*.—Acetone-δ-*d*-bornylsemicarbazone (85 g.) and 10% hydrochloric acid (850 c.c.) were heated on the water-bath for 1½ hours. δ-*Bornylsemicarbazide hydrochloride* crystallised on cooling and was recrystallised from alcohol after removal of a small quantity of di-*d*-bornylcarbamide by filtration (yield, 94%). The anhydrous substance, m. p. 190—198° (corr.), had $[\alpha]_D^{20}$ + 2·6° (c = 5 in dry alcohol) (Found in air-dried substance : loss at 105° in a vacuum, 14·1. $C_{11}H_{22}ON_3Cl,2H_2O$ requires H_2O, 12·7%. Found in anhydrous substance : C, 53·1; H, 8·9; Cl, 14·2. $C_{11}H_{22}ON_3Cl$ requires C, 53·3; H, 9·0; Cl, 14·3%).

δ-d-*Bornylsemicarbazide*.—δ-*d*-Bornylsemicarbazide hydrochloride (10 g.) dissolved in a little alcohol was treated with 8·5 c.c. of 20% sodium hydroxide solution and poured into water. The base was extracted with chloroform and obtained in needles by addition of light petroleum to the concentrated solution. The substance, dried in a vacuum at 50°, melted at 75° after softening some degrees lower, and had $[\alpha]_D^{20°}$ + 17·0° (c = 5 in dry alcohol). On keeping, it gradually decomposed (Found in dried substance : C, 62·5; H, 10·4. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0%).

δ-*d*-Bornylsemicarbazones of various ketones were prepared by adding the requisite quantity of ketone to a concentrated solution of the base in alcohol.

iso*Pulegone*-δ-d-*bornylsemicarbazone*, prepared from *iso*pulegone

having $\alpha_D^{18^\circ} - 6{\cdot}0^\circ$, crystallised in thick, rhombic plates, m. p. 224—226° (corr.), $[\alpha]_D^{20^\circ} + 9{\cdot}2^\circ$ ($c = 5{\cdot}04$ in chloroform) (Found: C, 72·8; H, 10·1. $C_{21}H_{35}ON_3$ requires C, 73·0; H, 10·2%).

4-*Methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone* crystallised in clusters of six-sided plates, softening slightly at 145° (corr.), melting at 154° (corr.), and having $[\alpha]_D^{20^\circ} + 27{\cdot}2^\circ$ ($c = 4{\cdot}898$ in dry alcohol) (Found: C, 70·5; H, 10·2. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%).

3-*Methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone*, prepared from optically inactive 3-methyl*cyclo*hexanone, melted at 172—177° (corr.) and had $[\alpha]_D^{20^\circ} + 27{\cdot}4^\circ$ ($c = 4{\cdot}85$ in dry alcohol) (Found: C, 70·5; H, 10·1. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%). Recrystallisation from alcohol or ligroin failed to resolve it into its components, even when seeded with d-3-*methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone*, m. p. 173—179° (corr.), $[\alpha]_D^{20^\circ} + 7{\cdot}4^\circ$ ($c = 4{\cdot}726$ in dry alcohol) (Found: C, 70·4; H, 10·1. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%), prepared from *d*-3-methyl*cyclo*hexanone kindly supplied by Dr. Kenyon.

Acetone-δ-d-neo*bornylsemicarbazone*, prepared in the same way as acetone-δ-*d*-bornylsemicarbazone, but at 190° in order to keep the *neo*bornylamine liquid, crystallised from alcohol in anhydrous needles, m. p. 175—179° (corr.), $[\alpha]_D^{20^\circ} - 92{\cdot}1^\circ$ ($c = 2{\cdot}008$ in dry alcohol) (Found: C, 66·6; H, 10·1. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 10·0%).

δ-d-neo*Bornylsemicarbazide hydrochloride* was prepared by hydrolysis of the above acetone derivative with dilute hydrochloric acid. The anhydrous substance melted at 198—202° (corr.) and had $[\alpha]_D^{20^\circ} - 50{\cdot}8^\circ$ ($c = 4{\cdot}982$ in dry alcohol) (Found in air-dried substance: loss at 105° in a vacuum, 5·3. $C_{11}H_{22}ON_3Cl,H_2O$ requires H_2O, 6·8%. Found in substance dried at 105° in a vacuum: Cl, 14·1. $C_{11}H_{22}ON_3Cl$ requires Cl, 14·3%).

δ-*d*-*neo*Bornylsemicarbazones were prepared by adding the requisite quantity of ketone to a concentrated solution of δ-*d*-*neo*-bornylsemicarbazide in alcohol.

4-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone* crystallised in rosettes of needles, m. p. 151—155° (corr.), $[\alpha]_D^{20^\circ} - 91{\cdot}3^\circ$ ($c = 2{\cdot}83$ in dry alcohol) (Found: C, 70·4; H, 10·0. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%).

3-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone*, prepared from optically inactive 3-methyl*cyclo*hexanone, melted at 157—161° (corr.) and had $[\alpha]_D^{20^\circ} - 91{\cdot}2^\circ$ ($c = 4{\cdot}772$ in dry alcohol) (Found: C, 70·6; H, 10·3. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2). Recrystallisation from alcohol or ligroin failed to resolve it into its components.

The author desires to express his thanks to Mr. R. E. Hedger for assistance in the work and to Dr. Kenyon for supplying the *d*-3-methyl*cyclo*hexanone used.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[*Received, July 16th*, 1927.]

CCLXIII.—*The Absorption Spectrum of Ergosterol in Relation to the Photosynthetic Formation of Vitamin* D.

By RICHARD ALAN MORTON, ISIDOR MORRIS HEILBRON, and EDWARD DAVID KAMM.

IT has been shown (Heilbron, Kamm, and Morton, *Biochem. J.*, 1927, **21**, 78) that the antirachitic potency developed on irradiation of ordinary cholesterol, either from cod-liver oil or from brain, may be traced to the presence in it of a minute quantity of some foreign substance which exhibits well-defined absorption bands near 293·5 μμ, 281·5μμ, and 270 μμ. These bands disappear on irradiation, concomitantly with the development of antirachitic potency in the product. A similar conclusion was almost simultaneously arrived at by Pohl (*Nach. Ges. Wiss. Göttingen*, 1926), using an entirely different spectroscopic technique (monochromatic light and photo-electric cells). These results are also substantiated by the fact that cholesterol regenerated from its dibromide could not be activated by irradiation with ultra-violet light. Subsequent work developed by using the spectroscopic method rapidly led to the conclusion that ergosterol—or a similar sterol—is the actual pro-vitamin, and this has been fully substantiated by animal tests (Rosenheim and Webster, *Biochem. J.*, 1927, **21**, 127; Windaus and Hess, *Nach. Ges. Wiss. Göttingen*, 1926).

In extension of our earlier work, it became necessary to examine in detail the absorption spectrum of ergosterol, in order to establish an accurate standard of comparison by means of which we could determine the relative richness of various materials in respect of the pro-vitamin.

In agreement with the work of Pohl as briefly reported by Windaus and Hess (*loc. cit.*), our results correspond in a very remarkable degree with the absorption curve found for ordinary cholesterol :

	λ max.	λ max.	λ max.
Cholesterol.....	293 μμ	280 μμ	269 μμ
Ergosterol	293·5 μμ	281·5 μμ	270 μμ

Further, the results indicate that ergosterol is 2—4 × 10^3 times as active as our specially prepared cholesterol (Heilbron, Kamm, and Morton, *loc. cit.*).

We next studied the change in the absorption spectrum brought about by irradiation of ergosterol in alcoholic solution. A solution of 0·05 g. of ergosterol in 250 c.c. of optically pure alcohol was prepared and portions were exposed to the light of a practically *new* (Hewittic) quartz mercury-vapour lamp of the vacuum type. Samples were withdrawn every 15 minutes and the absorption spectrum was determined. For this purpose two Hilger E_3 quartz spectrographs were used alternately, each being fitted with a rotating disc sector photometer. Two series of absorption curves were obtained showing the selective absorption at half-hour intervals. The two sets of curves were reasonably concordant and only one will therefore be described.

1. Ergosterol. Fresh solution not irradiated. Bands at 270 μμ, 281·5 μμ, and 293·5 μμ. Minimum 230 μμ. "ε" max. 10,200. "ε" min. 2,400.

2. Irradiated for 30 minutes. Broad maximum near 275 μμ. "ε" max. 8,500. Minimum near 230 μμ. "ε" min. 3,750. The absorption band is wider in the region 230—265 μμ than the corresponding band for the fresh solution.

3. Irradiated for 60 minutes. Broad maximum near 275 μμ. "ε" max. 7,150. Minimum near 230 μμ. "ε" min. 4,850. The curve shows a marked step-out in the region 240—260 μμ, indicating the incipient appearance of a band in that region of the spectrum.

4. Irradiated for 90 minutes. The curve shows a new maximum near 247 μμ. "ε" max. 6,300 and a minimum near 230 μμ. "ε" min. 5,800. The persistence of the new band is therefore low. At the same time the absorption curve shows marked absorption over the region 260—300 μμ, indicating that the ergosterol has not entirely disappeared.

5. Irradiated for 120 minutes. The band at 247 μμ has increased in persistence, whilst the absorption over the range 260—300 μμ shows a collateral decrease.

6. Irradiated 150 minutes. The band at 247 μμ is well developed. "ε" max. 5,250, a minimum is shown at 225 μμ, and the persistence is considerable. From 247 μμ—269 μμ the absorption curve is fairly straight, but at 270 μμ a sharp inflexion commences and the curve falls slowly to the limiting position near 310 μμ.

7. Irradiated for 6 hours. The solution is now almost diactinic and all trace of selective absorption has disappeared.

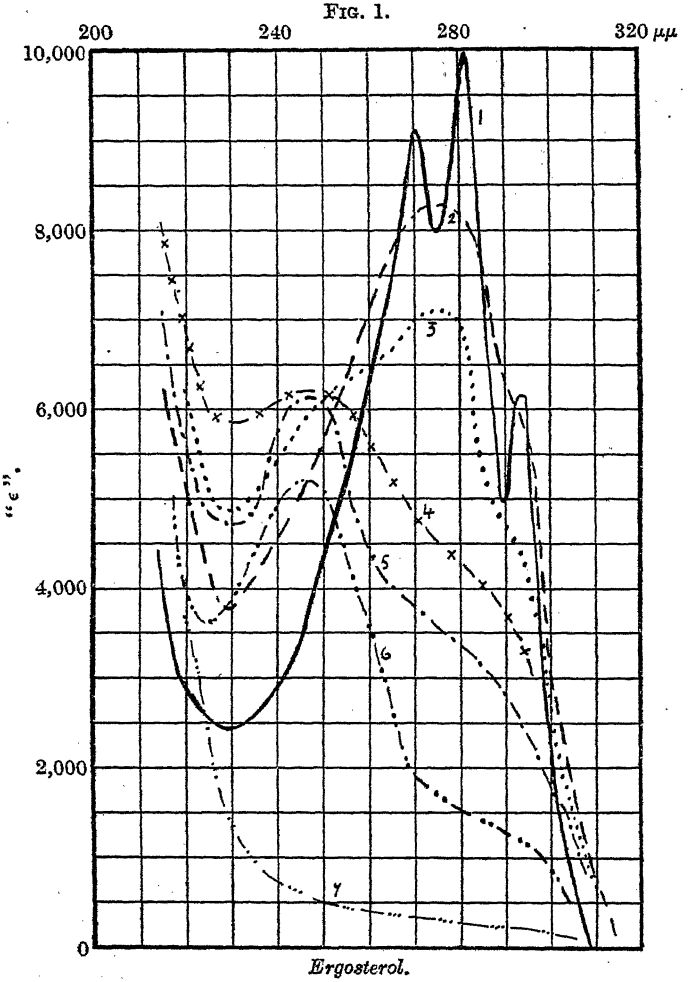
The curves (Fig. 1) show that the reaction

$$\text{ergosterol} \xrightarrow{\text{u.v. light}} \text{vitamin } D \quad . \quad . \quad . \quad . \quad (1)$$

is accompanied by the disappearance of selective absorption in the region 260—300 μμ and by the appearance of a new selective absorp-

tion in the region 230—260 μμ with a maximum at 247 μμ. This new band itself disappears with further irradiation, a fact which is

FIG. 1.

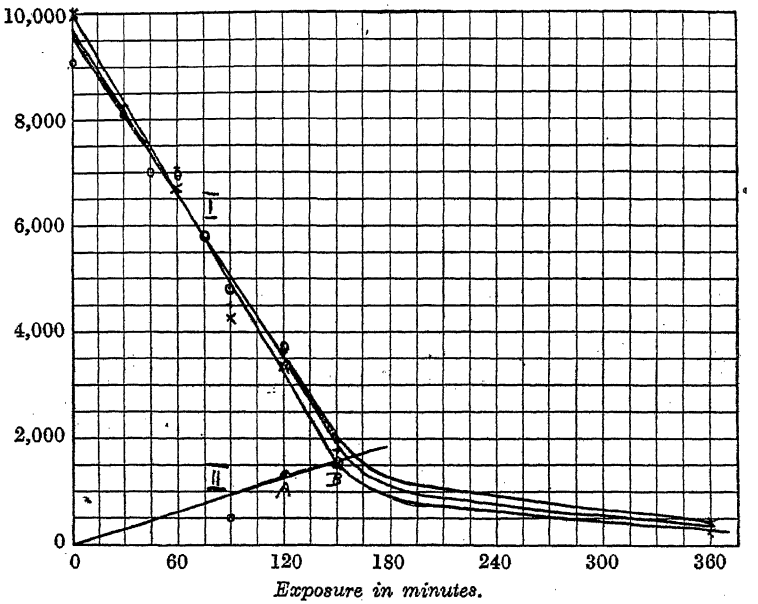


not inconsistent with the view that it is due to vitamin *D*, since it is known that "excessive" irradiation of cod-liver oil induces a loss of vitamin potency.*

* The results of biological experiments have now come to hand and show that the product giving the 247 μμ band at maximum intensity possesses very

When the extinctions at 270—275 μμ and 280 μμ are plotted against time, the result is, within experimental error, a straight line, indicating that the rate of disappearance of ergosterol depends solely on the energy input. By plotting the persistence of the new band against time, a roughly linear relation is likewise obtained (Fig. 2). These results can only mean that the *whole* of the incident energy is absorbed and is photochemically effective, within the absorption band and within the limits of the straight line relationship.

FIG. 2.



I, *extinction coefficients at* 281·5 μμ, 275 μμ, 270 μμ, *ergosterol curves.*
II, *persistence of new band* (*line* AB *produced cuts axes at origin*).

In our experience, the irradiation of thin layers of solid ergosterol is unsatisfactory. Complete disappearance of the original bands is secured only after long exposure and under conditions in which consecutive reactions are not precluded.

The absorption curves indicate a fact of considerable significance, namely, that the irradiation of ergosterol in solution or in the solid state is quite unlikely to give pure vitamin *D* unless special precautions are taken. The existence of a well-marked absorption

high antirachitic potency, whereas the product which has undergone irradiation until this band has disappeared is not effective at the same dosage. The tests were kindly carried out by Messrs. H. Jephcott and A. L. Bacharach, using the method described in their paper (*Biochem. J.*, 1926, **20**, 1351).

band between 225 μμ and 270 μμ characteristic of a photochemically unstable substance, *viz.*, vitamin *D*, means that if photodecomposition of this compound is to be avoided, *these radiations must be screened off*. The most suitable material for transmitting only light of the middle ultra-violet region is the proprietary "Vitaglass." Since, however, the rays between 270 and 293 μμ are absorbed to a considerable extent by vitaglass, very prolonged exposures will be necessary. Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 392) state that "the action of ultra-violet light on ergosterol leads to an obvious physical change and the production of a yellowish resin." The nature of the intramolecular change which gives rise to the vitamin formation is at present unknown. The first step towards solving this problem is the preparation of pure vitamin *D*, and at present the line of attack most clearly indicated is the prevention of its photochemical decomposition by suitable screening.

The present results have a very definite bearing on the problem of the industrial production of vitamin *D*. Anything approaching a satisfactory yield in the reaction (1) requires prolonged irradiation —an expensive process. Screening a quartz mercury-vapour lamp with vitaglass is obviously wasteful, since the large energy emission of the 265 μμ and 253·6 μμ (resonance) lines is detrimental to the stability of vitamin *D*, and must not have access to the solution undergoing irradiation. It would seem, therefore, that the mercury vapour lamp is unsuitable for this particular photochemical reaction.

The alternative light sources are carbon or metal arcs. It is quite feasible to obtain suitably treated carbon arcs with little or no emission on the ultra-violet side of 270 μμ. On the other hand, there can be little doubt that the working cost of mercury vapour lamps is lower than that of carbon or tungsten arcs producing the same intensity of ultra-violet light of all wave-lengths. These considerations show that the photochemical formation of vitamin *D* in good yield presents a formidable problem both to research and to costing. There seems, however, every reason to expect a solution if the experiments are accurately controlled by spectroscopic means.

Some comment is necessary on a statement by Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 395) to the effect that the absorption of ergosterol "extends well into the ultra-violet region of sunlight." The facts appear to be as follows. Dorno found that the limiting detectable ultra-violet wave-lengths of sunlight were: December—February, 3120 Å.; September—November, 3080 Å.; March—May, 3010 Å.; June—August, 2962 Å.; the relative intensities being Jan. 100, April 400, July 1000, October 600.

Only a very small area of the ergosterol absorption is covered by wave-lengths on the long-wave side of 2960 Å., and appreciable

photochemical reaction only appears possible in summer sunlight. This is, of course, in harmony with the seasonal incidence of rickets.

A brief remark on the paper by Hume, Lucas, and Smith (*Biochem. J.*, 1927, **21**, 362) is also necessary. These authors suggest that the mechanism of synthesis of vitamin *D in vivo* is the photochemical transformation of traces of ergosterol or a substance with similar absorption bands. Unfortunately, the transmission of epidermis falls to zero near 296 μμ, so that a direct experimental test is excluded. We propose to investigate the matter further in two ways :

(1) To ascertain spectroscopically whether ergosterol, in solution in a quartz vessel, can be transformed into vitamin *D* by exposure to sunlight.

(2) To ascertain whether an extract containing ergosterol can be prepared from skin by means of solvents.

During the course of this work preliminary attempts were made to ascertain whether the formation of vitamin *D* is due to polymerisation. Determinations of molecular weight by the Rast micro-method failed to establish any such change, but we were not completely satisfied with the conditions under which the determinations were carried out and are repeating and extending the experiments.*

We desire to express our thanks to Mr. W. Doran and Mr. M. N. Leathwood for help in the experimental work, to Mr. F. H. Carr, C.B.E., of British Drug Houses, Ltd., for the ergosterol, and to the Food Investigation Board for a grant which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, May 27th*, 1927.]

CCLXIV.—*Studies in the Coumarin Series. Part I. The Action of the Grignard Reagent upon Substituted Coumarins.*

By ISIDOR MORRIS HEILBRON and DOUGLAS WILLIAM HILL.

DECKER and FELLENBERG (*Annalen*, 1907, **356**, 281) have shown that the interaction of coumarins and the Grignard reagent leads, under carefully specified conditions, to the production of mono-alkyl- or -aryl-pyrylium salts, and more recently Willstätter and his

* Whilst this paper was in the press, our attention was drawn to a paper by Pohl (*Nach. Ges. Wiss. Göttingen*, Mathematisch-Physikalische Klasse, 1927) in which the absorption curves of ergosterol and vitamin *D* are described. The photoelectric and photographic methods are in substantial agreement.

co-workers (*Ber.*, 1924, **57**, 1938, 1945) have used this reaction for the synthesis of anthocyanidins from 3-methoxycoumarins. On the other hand, Houben (*Ber.*, 1904, **37**, 498) has described the formation of dialkyl and diaryl derivatives of coumarin itself. Whereas magnesium alkyl halides led to the formation of 2 : 2-dialkyl-Δ^3-chromens, magnesium phenyl bromide gave rise to the carbinol (I), the formation of which he attributed to a steric hindrance preventing the loss of water necessary for the production of the 2 : 2-diphenylchromen.

The work described in the present paper was initially undertaken with the intention of synthesising flavylium chlorides containing methoxyl or hydroxyl in the 4-position; the latter would probably readily lose hydrogen chloride and pass into flavones. As, however, only diaryl products were obtained, a detailed investigation of coumarins substituted in the 3- and 4-positions was initiated which has led to the isolation of three distinct types of product. Two of these, differently constituted diarylchromens, are now described; the third, a series of benzopyrylium salts, will form the subject of a subsequent communication. While this work was in progress, a most noteworthy contribution to the subject was published by Löwenbein (*Ber.*, 1924, **57**, 1517), who showed that the supposed diphenyl-*o*-hydroxystyrylcarbinol (I) of Houben is in reality 2 : 4-diphenylchroman-2-ol (II), which readily loses water on heating with glacial acetic acid, yielding 2 : 4-diphenyl-Δ^2-chromen (III).

(I.) $C_6H_4<^{CH:CH\cdot CPh_2\cdot OH}_{OH}$ $\qquad$ $C_6H_4<^{CHPh\cdot CH_2}_{O\text{——}CPh\cdot OH}$ (II.)

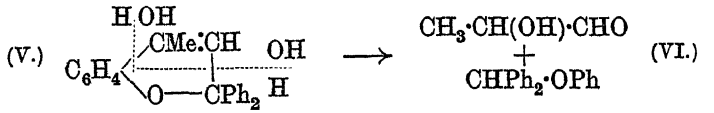
In addition to the chromanol, he obtained a second compound which proved to be 2 : 2-diphenyl-Δ^3-chromen (IV).

(III.) $C_6H_4<^{CHPh\cdot CH}_{O\text{——}CPh}$ $\qquad$ $C_6H_4<^{CH:CH}_{O\text{——}CPh_2}$ (IV.)

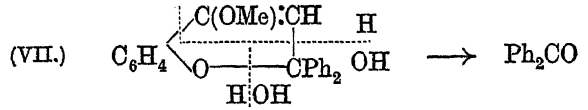
Löwenbein also examined the 5 : 7-, 4 : 6-, and 4 : 7-dimethylcoumarins, all of which, according to him, yielded the corresponding chromanols analogous to (II).

In the course of our own experiments, the action of magnesium phenyl bromide upon both 3-methyl- and 3-phenyl-coumarin was studied. In each case the corresponding chromanol was isolated, from which the elements of water were readily eliminated on heating with glacial acetic acid, 2 : 4-diphenyl-3-methyl-Δ^2-chromen and 2 : 3 : 4-triphenyl-Δ^2-chromen, respectively, being formed. Since these compounds were prepared, a full description of the latter has been published by Löwenbein and Rosenbaum (*Annalen*, 1926, 448, 223), who have prepared it both from 3-phenylcoumarin and

by the interaction of magnesium phenyl bromide upon 2 : 3-diphenylbenzopyrylium perchlorate.*



On the other hand, 4-methyl- and 4-methoxy-coumarins yield 2 : 2-*diphenyl*-4-*methyl*-Δ^3-*chromen* (V) and 4-*methoxy*-2 : 2-*diphenyl*-Δ^3-*chromen* (VII), respectively.



According to Löwenbein (*loc. cit.*), certain Δ^3-chromens are converted into coumarone derivatives of the same empirical formula on boiling with glacial acetic acid. Neither of the above compounds (V and VII) was altered under such conditions. That, however, they are in reality Δ^3-chromens has been definitely established by a study of their products of hydrolysis. 2 : 2-Diphenyl-4-methyl-Δ^3-chromen was refluxed for 24 hours with 50% potassium hydroxide solution; ring scission then occurred with production of *benzhydryl phenyl ether* (VI). With 4-methoxy-2 : 2-diphenyl-Δ^3-chromen, refluxing for 5 hours with 33% potassium hydroxide solution was sufficient to cause complete scission. The product isolated in this case was benzophenone, cleavage occurring in the same manner as found by Baker (J., 1925, **127**, 2349). These results, although not wholly in agreement with Löwenbein's findings in the case of the 4 : 6- and 4 : 7-dimethylcoumarins, harmonise well with the work of Kohler (*Amer. Chem. J.*, 1907, **38**, 511), who has shown that addition of the Grignard reagent to $\alpha\beta$-unsaturated ketones takes place both in the 1 : 2 and in the 1 : 4 positions, the relative amounts of each compound formed being dependent on the nature of the unsaturated compound; *e.g.*, the unsaturated ketone $C_6H_5\cdot CH{:}CH\cdot CO\cdot C_6H_5$ gives mainly 1 : 4 addition (94—96%), whereas $(C_6H_5)_2C{:}CH\cdot CO\cdot C_6H_5$ yields 100% of unsaturated alcohol owing to complete 1 : 2 addition.

Our experiments with coumarins have led us to the definite conclusion that the primary reactions with the Grignard reagent follow a common course, the ultimate formation of a Δ^2- or Δ^3-chromen being influenced solely by the position of the substituent

* Dr. Löwenbein informs me (private communication) that he has also prepared 2 : 4-diphenyl-3-methyl-Δ^2-chromen (m. p. 94°) by the decomposition of 2-phenyl-3-methylbenzopyrylium perchlorate with magnesium phenyl bromide—I. M. H.

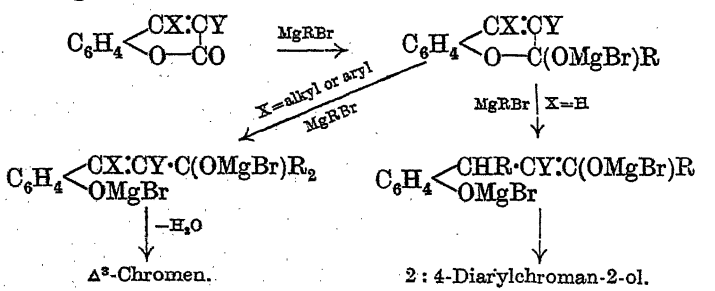
in the pyran ring. Two explanations may be presented to meet the above postulation. In the first place, the primary reaction involving one molecule of the Grignard reagent may result in the production of an αβ-unsaturated ketone (VIII) and the subsequent

(VIII.) $C_6H_4<^{CX:CH\cdot COR}_{OMgBr}$ $C_6H_4<^{CHR\cdot CH:CR\cdot OH}_{OH}$ (IX.)

reactions would then directly follow the Kohler rule. Where X = hydrogen, 1 : 4 addition would chiefly occur with production of the enol (IX), from which the chromanol (X) would result, as pointed out by Löwenbein (*Ber.*, 1924, **57**, 1517), through intra-

(X.) $C_6H_4<^{CHR\cdot CH_2}_{O\text{——}CR\cdot OH}$ $C_6H_4<^{CX:CH\cdot CR_2\cdot OH}_{OH}$ (XI.)

molecular rearrangement from the keto-form. On the other hand, where X is other than hydrogen, 1 : 2 addition will take place, giving the styrylcarbinol (XI), which will immediately pass into the Δ^3-chromen by loss of a molecule of water. Löwenbein considers, however, that Δ^3-chromen formation occurs directly without opening of the lactone ring, since phenyl *o*-hydroxystyryl ketone yields only 2 : 4-diphenylchroman-2-ol when treated with magnesium phenyl bromide, whereas, as previously mentioned, coumarin gives both the chromanol and the Δ^3-chromen. It will be conceded, however, that the reactions involved with the two compounds are not identical and that the presence of the free *o*-hydroxyl group in the ketone may well favourably influence the 1 : 4 addition. An alternative mechanism differing only in degree from the above, and equally explicable on the Kohler rule, may also be reached by assuming that the first reaction with the Grignard reagent comprises direct addition without ring opening. The course of the subsequent reactions under these conditions is expressed by the following formulæ :

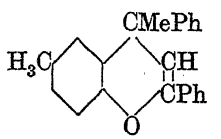


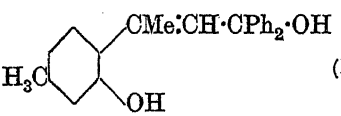
Either explanation provides a perfectly general interpretation of the Δ^2- or Δ^3-diarylchromen formation and meets the problem presented by the 3-substituted coumarins which fail to yield

Δ^3-diarylchromens, a result incompatible with the idea that interaction can occur directly without scission of the lactone ring. The fact that whereas coumarin itself gives both the 1 : 4- and 1 : 2-addition products, whilst the 3-substituted coumarins give only 1 : 4-addition, is also in agreement with Kohler's findings in the case of the unsaturated ketones $C_6H_5 \cdot CH{:}CMe \cdot CO \cdot C_6H_5$ and $C_6H_5 \cdot CH{:}CPh \cdot CO \cdot C_6H_5$.

The complete harmony between our experimental results and these theoretical deductions induced us to re-examine the products obtained from both 4 : 6- and 4 : 7-dimethylcoumarin, which, according to Löwenbein, yielded 2 : 4-diphenylchroman-2-ol derivatives. Working in exact accordance with this author's conditions, we failed to obtain from 4 : 6-dimethylcoumarin any trace of the so-called chromanol, m. p. 110°, but isolated in good yield a substance, m. p. 127°, which corresponded to the compound obtained by Löwenbein by treatment of the chromanol with glacial acetic acid and to which he assigned the structure of 2 : 4-diphenyl-4 : 6-dimethyl-Δ^2-chromen (XII). The main yield from 4 : 7-dimethylcoumarin was a compound, m. p. 86°, apparently identical with the supposed 2 : 4-diphenyl-4 : 7-dimethyl-Δ^2-chromen (m. p. 87°). In addition, a very small yield of a substance, m. p. 146°, was obtained of empirical formula $C_{23}H_{22}O_2$, corresponding to the supposed 2 : 4-diphenyl-4 : 7-dimethylchroman-2-ol of m. p. 144°.

(XII.)





(XIII.)

The fact that chromens were obtained directly from the products of the reaction is in itself some indication that these do not belong to the Δ^2-series, and this we have proved by an examination of their scission products. Benzhydryl *p*-tolyl ether was obtained in good yield from the 4 : 6-dimethyl compound. In the case of 2 : 2-diphenyl-4 : 7-dimethyl-Δ^3-chromen, in addition to benzhydryl *m*-tolyl ether, lactaldehyde, m. p. 105°, was isolated, thus definitely establishing the constitution of these compounds as diaryl-Δ^3-chromens.

The substance, m. p. 146°, is probably the intermediate *diphenyl-2-hydroxy-β : 4-dimethylstyrylcarbinol* (XIII), but the quantity at our disposal did not allow of detailed examination.

We acknowledge our indebtedness to Dr. A. Löwenbein, with whom we have been in communication concerning the mechanism of the changes involved in these reactions, and who has freely given us the advantage of his views.

EXPERIMENTAL.

4-Hydroxy-2 : 2-diphenyl-Δ^3-chromen.—Magnesium phenyl bromide (prepared from bromobenzene, 14·5 g., magnesium turnings, 2·5 g., and ether, 100 c.c.) was added to 4-hydroxycoumarin (5 g.), suspended in benzene (250 c.c.). A solid was rapidly precipitated which did not redissolve after 5 hours' heating under reflux. The reaction mixture was decomposed by ice-cold, dilute hydrochloric acid, unchanged bromobenzene and diphenyl were removed by steam distillation, and the residual solid was separated from unacted-upon 4-hydroxycoumarin by boiling with water, in which the latter was readily soluble. After drying, the *chromen* was crystallised from benzene and then twice from absolute alcohol, from which it separated in colourless needles, m. p. 230—231°. It is strongly acidic and dissolves readily in sodium hydroxide and sodium carbonate solutions; it gives no coloration with ferric chloride (Found: C, 83·9; H, 5·1. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

4-Methoxy-2 : 2-diphenyl-Δ^3-chromen (VII).—This was prepared in an analogous manner by the action of magnesium phenyl bromide (from 14 g. of bromobenzene) upon a solution of 4-methoxycoumarin (5 g.) in dry benzene (200 c.c.). The residue left after steam distillation was filtered off, dried, and twice recrystallised from absolute alcohol, the *chromen* being obtained in colourless plates, m. p. 135° (yield, 7 g.) (Found: C, 84·1; H, 5·5. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%). It is readily soluble in the usual organic solvents.

Hydrolysis.—The chromen (2 g.) was heated under reflux with 33% potassium hydroxide solution (25 c.c.) for 5 hours. After dilution with water, the whole was extracted with ether, and the oil isolated from the extract was treated with hydroxylamine. The solid thus obtained, after crystallisation from alcohol, melted at 139° and was shown to be identical with benzophenoneoxime by a mixed melting point with an authentic specimen.

4-Methoxy-2 : 2-dianisyl-Δ^3-chromen, prepared from magnesium *p*-anisyl bromide by the method previously described, crystallised from benzene in colourless needles, m. p. 155° (Found: C, 76·8; H, 6·0. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%).

2 : 2-Diphenyl-4-methyl-Δ^3-chromen (V).—This was prepared by treating a solution of 4-methylcoumarin (10 g.) in benzene (150 c.c.) with magnesium phenyl bromide (bromobenzene, 30 g.) in dry ether (100 c.c.). After boiling under reflux for 4 hours on the water-bath, the whole was steam-distilled and the residue extracted with ether. After removal of the solvent from the dried extract, crystals contaminated with some oily material were obtained. The oil was removed by treatment with a small quantity of alcohol, and the yellow solid recrystallised from benzene and again from glacial

acetic acid; the *chromen* then separated in colourless prisms, m. p. 89° (Found: C, 88·7; H, 6·4. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1%).

Hydrolysis. Isolation of benzhydryl phenyl ether (VI). The above chromen (0·5 g.) was gently boiled under reflux with 50% potassium hydroxide solution (15 c.c.) for 24 hours. After cooling, the reaction mixture was extracted with ether. The oil left after removal of the solvent from the washed and dried extract solidified on standing and then crystallised from a very small volume of light petroleum in colourless needles, m. p. 56°. The compound was insoluble in aqueous sodium hydroxide and gave no colour reaction with ferric chloride (Found: C, 88·0; H, 6·4. $C_{19}H_{16}O$ requires C, 87·8; H, 6·2%).

2 : 2-*Diphenyl*-4 : 6-*dimethyl*-Δ^3-*chromen*.—The Grignard reaction in this case was carried out in a similar manner to that described by Löwenbein (*loc. cit.*) by the slow addition of magnesium phenyl bromide (from bromobenzene, 14 g.) to a hot solution of 4 : 6-dimethylcoumarin (5 g.) in benzene (120 c.c.). The reaction mixture was then heated on the water-bath for ½ hour, decomposed by means of cold ammonium chloride solution, and steam-distilled to remove bromobenzene and diphenyl. The residue, which became solid after 24 hours, was then separated and rubbed with a small quantity of ether, which induced it to crystallise. The product was recrystallised from alcohol, separating in colourless rhombs, m. p. 126°. The ether used to crystallise the residue from the steam distillation deposited more of the same compound (Found: C, 88·3; H, 6·5. $C_{23}H_{20}O$ requires C, 88·4; H, 6·4%).

Hydrolysis. Isolation of benzhydryl p-*tolyl ether*. The chromen (2 g.) was gently boiled under reflux with potassium hydroxide solution (25 g. in 25 c.c. of water) for 24 hours. After cooling, the yellow, alkaline solution, together with some solid material, was extracted with ether, and the extract was well washed with water, dried, and evaporated. The residual solid crystallised from 90% alcohol (animal charcoal) in colourless rhombs, m. p. 96°, which were insoluble in sodium hydroxide solution (Found: C, 87·8; H, 5·9. $C_{20}H_{18}O$ requires C, 87·6; H, 5·8%).

Diphenyl-2-*hydroxy*-β : 4-*dimethylstyrylcarbinol* (XIII).—4 : 7-Dimethylcoumarin was treated with magnesium phenyl bromide as was the 4 : 6-isomeride. The resinous product from the steam distillation was dried between porous tiles and then vigorously scratched with ether, whereupon it crystallised. The crystalline mass so obtained was filtered off and twice recrystallised from 90% alcohol, from which the *carbinol* separated in colourless needles, m. p. 146° (yield, 10%) (Found: C, 83·4; H, 6·4. $C_{23}H_{22}O_2$ requires C, 83·6; H, 6·6%).

2 : 2-*Diphenyl*-4 : 7-*dimethyl*-Δ^3-*chromen*.—This compound was obtained in two ways : (*a*) The ethereal filtrate after removal of the preceding carbinol deposited, on slow evaporation, a large quantity of a solid, which crystallised from alcohol in colourless needles, m. p. 86° (yield, 75%). (*b*) Diphenyl-2-hydroxy-β : 4-dimethylstyrylcarbinol (1 g.) was heated under reflux for 1 hour with glacial acetic acid (20 c.c.). The gummy residue obtained on dilution with water was crystallised from alcohol, yielding glistening, colourless needles, m. p. 87°, identical with the product in (*a*) (Found : C, 88·3; H, 6·7. $C_{23}H_{20}O$ requires C, 88·4; H, 6·5%).

Isolation of Benzhydryl m-*Tolyl Ether*.—This hydrolysis was carried out in three ways : (*a*) As in previous cases, the chromen (2 g.) was heated for 24 hours with potassium hydroxide solution (25 g. in 25 c.c. of water). The crude product crystallised from alcohol in colourless needles, m. p. 125°. (*b*) The chromen (2 g.) was heated with potassium hydroxide (15 g. in 25 c.c. of water) at 180° in an autoclave for 4 hours. The product was washed with water (200 c.c.), and the solid crystallised twice from 75% alcohol in presence of animal charcoal. It was thus obtained in colourless needles identical with those in (*a*). (*c*) The chromen (1 g.) was fused with potassium hydroxide (10 g.) and, when cold, the mass was dissolved in water and extracted with ether. After purification, the substance described in (*a*) and (*b*) was obtained (Found : C, 87·4; H, 5·9. $C_{20}H_{18}O$ requires C, 87·6; H, 5·8%).

The alkaline solution from (*c*) was rendered acid, and the solution, which contained a small quantity of solid material, was extracted with ether. After removal of the solvent, the residue crystallised from a small volume of methyl alcohol in colourless needles, m. p. 103—105°. It readily reduced Fehling's solution and Tollens's reagent and was identical with lactaldehyde in all respects.

2 : 4-*Diphenyl*-3-*methylchroman*-2-*ol*.—3-Methylcoumarin (10 g.), dissolved in benzene, was heated for 4 hours on the water-bath with magnesium phenyl bromide (3 mols.). The reaction mixture was decomposed with dilute hydrochloric acid and steam-distilled. The non-volatile residue was collected and crystallised from alcohol and finally from benzene, from which the *chromanol* separated in colourless crystals, m. p. 149° (Found : C, 83·9; H, 6·1. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%).

2 : 4-*Diphenyl*-3-*methyl*-Δ^2-*chromen* was prepared by boiling the above chromanol (1·5 g.) with glacial acetic acid (10 c.c.) for 1 hour. The cold solution was diluted with water, and the precipitate crystallised from alcohol, the *chromen* separating in colourless needles, m. p. 91° (Found : C, 88·5; H, 6·2. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1%).

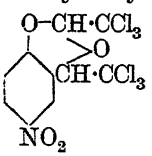
In conclusion, we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (D. W. H.) which has enabled this research to be carried out.

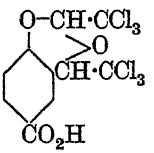
THE UNIVERSITY, LIVERPOOL. [*Received, June 8th*, 1927.]

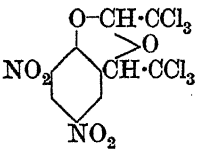
CCLXV.—*The Condensation of Chloral with Phenol.*

By FREDERICK DANIEL CHATTAWAY and ALEXANDER ALLAN MORRIS.

IT has been shown recently (J., 1926, 2720; this vol., p. 685) that in presence of concentrated sulphuric acid, chloral reacts readily with *p*-nitrophenol and with *p*-hydroxybenzoic acid, yielding respectively anhydro-5-nitro- (I) and anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (II)


(I.)

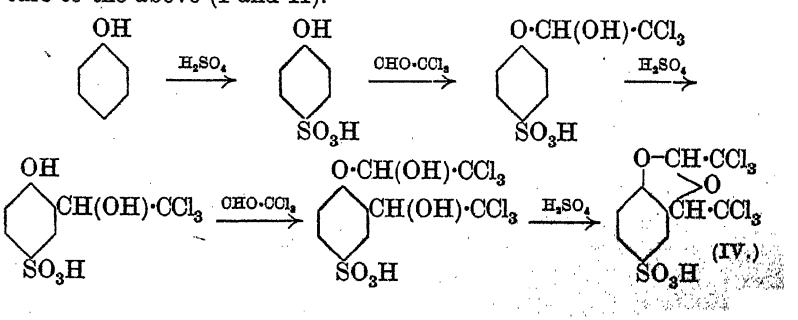

(II.)


(III.)

Chloral appears to condense in this way only with phenols in which the hydrogen in the para-position to the hydroxyl has been replaced by other groups.

When phenol itself is added to chloral suspended in concentrated sulphuric acid, an immediate reaction occurs, and an oily liquid separates which rapidly changes into an opaque, white solid. This readily dissolves in alcohol, giving a colourless solution from which nothing crystallises on cooling. On evaporating off the solvent, a viscid liquid is left which solidifies to a colourless, transparent, resin-like mass, the constitution of which has not yet been determined.

If, however, the phenol is first dissolved in the sulphuric acid, whereby *p*-phenolsulphonic acid is formed, this on addition of chloral slowly reacts, forming a compound (IV) analogous in structure to the above (I and II).

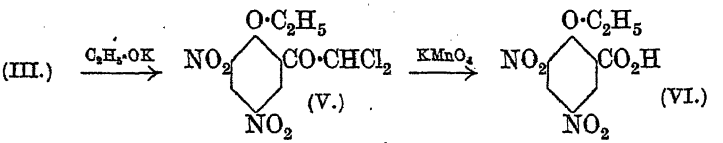

(IV.)

This compound behaves in all respects as a normal sulphonic acid. It is a colourless solid with no definite melting point. It crystallises with three molecules of water, two of which can be removed by heating, and forms well-crystallised salts. When acted upon by phosphorus pentachloride, it forms a *sulphonyl chloride*. This with ethyl and methyl alcohol yields *esters*, with ammonia a *sulphonamide*, and with aniline a *sulphonanilide*.

Its constitution is similar to that of the condensation product (I) yielded by *p*-nitrophenol, since both compounds on nitration yield *anhydro*-3 : 5-*dinitro*-2-ββ*β*-*trichloro*-α-*hydroxyethoxy*-1-ββ*β*-*trichloro*-α-*hydroxyethylbenzene* (III).

The molecules of water are probably attached to the sulphonic residue, the anhydride ring remaining unbroken, since, although only two are removed by heating, yet the ammonium salt is obtained in the anhydrous condition.

The constitution of the acid is further confirmed by the product of the action of alcoholic potash on the dinitro-derivative (III), whereby ωω-*dichloro*-3 : 5-*dinitro*-2-*ethoxyacetophenone* (V) is formed, which on oxidation by potassium permanganate yields 3 : 5-dinitro-2-ethoxybenzoic acid (VI).



Experimental.

Anhydro-2-ββ*β*-*trichloro*-α-*hydroxyethoxy*-1-ββ*β*-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonic Acid* (IV).—Phenol (100 g.; 1 mol.) was added slowly to 1000 c.c. of well-cooled sulphuric acid (*d* 1·8). After an hour, 400 g. of chloral hydrate (2 mols. + 50 g. excess) were gradually added with constant stirring. The mixture was then kept at the ordinary temperature for 4 days with occasional vigorous shaking. Reaction slowly took place, a bulky, white solid separating in the body of the solution, whilst a solid crust of metachloral formed on the surface. The solid products were filtered off on asbestos, and extracted with boiling water until the filtrate no longer deposited crystals when cooled and strongly acidified. The *sulphonic acid* was thus separated from the metachloral, which was left as a white solid insoluble in boiling water. The filtered aqueous extracts were mixed and evaporated until oily streaks appeared on the surface of the boiling liquid. On cooling, the sulphonic acid separated in viscid oily drops which crystallised into a mass of very thin, lustrous plates (yield, 150 g.). The sulphonic

acid is moderately easily soluble in boiling benzene and separates from this solution in very thin, colourless, lustrous, irregular plates containing three molecules of water (Found: C, 23·75; H, 2·3; Cl, 42·2. $C_{10}H_6O_5Cl_6S,3H_2O$ requires C, 23·8; H, 2·4; Cl, 42·1%).

When heated, the trihydrated acid partly liquefies between 125° and 130°, small prismatic crystals of a monohydrated acid separating.

When heated for ½ hour at 110°, the acid loses two molecules of water, leaving a crystalline aggregate of small, colourless, prismatic crystals of the monohydrated acid (Found: Loss of water at 110°, 7·0. $C_{10}H_6O_5Cl_6S,3H_2O \longrightarrow H_2O$ requires loss of water, 7·1%).

The monohydrated acid is very easily soluble in alcohol and acetone, and very sparingly soluble in boiling benzene and chloroform. It can be recrystallised by dissolving it in boiling acetic acid and adding concentrated hydrochloric acid a little at a time until the solution shows a slight turbidity. On cooling, the acid separates in small, colourless prisms which melt with decomposition between 150° and 166° (Found: C, 25·5; H, 1·7; Cl, 45·3; S, 7·0. $C_{10}H_6O_5Cl_6S,H_2O$ requires C, 25·6; H, 1·7; Cl, 45·4; S, 6·85%).

When moistened with a little cold water, the crystals of the monohydrated acid swell up into an amorphous sticky mass, which on warming gives a clear solution from which the hydrated acid crystallises on addition of a little concentrated hydrochloric acid.

It forms an anhydrous *ammonium* salt which crystallises from a dilute aqueous solution of ammonia in very small, colourless prisms (Found: C, 25·9; H, 2·0; Cl, 45·5. $C_{10}H_9O_5NCl_6S$ requires C, 25·65; H, 1·9; Cl, 45·5%).

Nitration of Anhydro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene-5-sulphonic Acid.—The sulphonic acid (40 g.) was added to a mixture of 150 c.c. of nitric acid (*d* 1·5) and 5 c.c. of concentrated sulphuric acid and heated to boiling. After cooling, the brown solution was poured on crushed ice; the dinitro-compound (III) then separated as a greenish-white solid, which, after drying, was recrystallised from boiling alcohol.

A product similar in every way was obtained when anhydro-5-nitro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene was nitrated in the same manner.

Anhydro-3:5-dinitro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene (III) is easily soluble in boiling acetic acid, alcohol, acetone, and benzene, and crystallises from all these solvents in two polymorphic modifications. On cooling, a solution of the compound in about three times its weight of boiling alcohol the labile modification first separates as slender, silky needles. On allowing these to stand in the mother-liquor, pale yellow rhombohedra of the stable form appear and grow at the expense of the labile form,

which dissolves and finally disappears. Both forms melt at 163° (Found: N, 6·0; Cl, 46·1. $C_{10}H_4O_6N_2Cl_6$ requires N, 6·1; Cl, 46·2%).

The position of the second nitro-group in this compound was established by its behaviour with alcoholic potash. The finely powdered dinitro-compound (25 g.) was gradually added to a solution of 30 g. of potassium hydroxide in 400 c.c. of alcohol, well cooled in a freezing mixture; it dissolved, giving a deep red solution, and chloroform was produced. After about 15 minutes, the liquid was neutralised by hydrochloric acid and the alcohol distilled off in a current of steam; *ωω-dichloro*-3 : 5-*dinitro*-2-*ethoxyacetophenone* (V) then separated as a liquid, which on cooling solidified to a crystalline, yellow mass (17·5 g.). It is readily soluble in boiling alcohol, from which it separates in small, yellow prisms, m. p. 82—84°, which darken when exposed to strong sunlight (Found: N, 8·7; Cl, 22·2. $C_{10}H_8O_6N_2Cl_2$ requires N, 8·7; Cl, 22·0%).

It yields an *osazone*,

$$OEt\cdot C_6H_2(NO_2)_2\cdot C(:N\cdot NH\cdot C_6H_3Cl_2)\cdot CH:N\cdot NH\cdot C_6H_3Cl_2,$$

when heated with an alcoholic solution of 3 : 5-dichlorophenylhydrazine. This compound is very sparingly soluble in boiling chloroform, from which it separates in minute, orange needles, m. p. 224° (Found: N, 14·4; Cl, 24·6. $C_{22}H_{16}O_5N_6Cl_4$ requires N, 14·3; Cl, 24·2%).

Oxidation of ωω-Dichloro-3 : 5-*dinitro*-2-*ethoxyacetophenone by Permanganate.*—ωω-Dichloro-3 : 5-dinitro-2-ethoxyacetophenone (15 g.) was added to a hot aqueous solution of 15 g. of potassium permanganate, and boiled until the oily drops first formed on the addition of the compound disappeared. The deep yellow filtrate from the precipitated manganese dioxide was concentrated, and an excess of hydrochloric acid added; 3 : 5-dinitro-2-ethoxybenzoic acid then separated, m. p. 132·5° (compare Ullmann, *Annalen*, 1909, **336**, 85) (Found: C, 42·6; H, 3·3; N, 10·9. Calc. for $C_9H_8O_7N_2$: C, 42·2; H, 3·1; N, 10·9%).

Anhydro-2-*ββββ-trichloro*-α-*hydroxyethoxy*-1-*ββββ-trichloro*-α-*hydroxyethylbenzene*-5-*sulphonyl Chloride*, $O<\begin{matrix}CH(CCl_3)\cdot O\\CH(CCl_3)\end{matrix}>C_6H_3\cdot SO_2Cl$.—The monohydrated acid (30 g.) and powdered phosphorus pentachloride (55 g.) were heated on the water-bath for 5 minutes, and the viscous pale brown oil formed was poured slowly over crushed ice. The *sulphonyl chloride* separated as a white solid, and crystallised from ether–light petroleum in very slender, colourless needles, m. p. 130·5° (Found: C, 25·5; H, 1·3; Cl, 52·6. $C_{10}H_5O_4Cl_7S$ requires C, 25·6; H, 1·1; Cl, 52·9%).

When boiled with any alcohol it reacts readily and yields the corresponding alkyl sulphonate. The *methyl* ester separates from

boiling methyl alcohol, in which it is moderately easily soluble, in small, highly refracting, colourless prisms, m. p. 150° (Found: C, 28·3; H, 1·7; Cl, 45·7. $C_{11}H_8O_5Cl_6S$ requires C, 28·4; H, 1·7; Cl, 45·8%). The *ethyl* ester separates from boiling ethyl alcohol in small, colourless, elongated, irregular plates, m. p. 143° (Found: C, 29·4; H, 2·2; Cl, 44·5. $C_{12}H_{10}O_5Cl_6S$ requires C, 30·1; H, 2·1; Cl, 44·4%).

The sulphonyl chloride also reacts readily with ammonia and with aniline in boiling alcohol to form a sulphonamide and a sulphonanilide.

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonamide* separates from boiling alcohol, in which it is readily soluble, in colourless, small, silvery plates, m. p. 207° (Found: N, 3·2; Cl, 47·3. $C_{10}H_7O_4NCl_6S$ requires N, 3·1; Cl, 47·3%).

When dissolved in acetic acid and chlorinated, it yields *anhydro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphondichloroamide*, which dissolves easily in chloroform and separates in colourless, slender prisms, m. p. 165—174° (decomp.) (Found: Cl as $\cdot NCl_2$, 13·4. $C_{10}H_5O_4NCl_8S$ requires Cl as NCl_2, 13·7%).

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonanilide* crystallises from dilute alcohol in very slender, silky, hair-like prisms, m. p. 168·5° (Found: N, 2·7; Cl, 40·5. $C_{16}H_{11}O_4NCl_6S$ requires N, 2·7; Cl, 40·5).

THE QUEEN'S COLLEGE, OXFORD. [*Received June 24th*, 1927.]

NOTES

Co-ordination Compounds of Beryllium and m- *and* p-*Nitrobenzoylacetone.* By HENRY BURGESS.

THE mutarotation of beryllium benzoylcamphor was attributed to an asymmetric arrangement around the beryllium atom by Lowry and Burgess (J., 1924, **125**, 2082), but owing to the occurrence of two asymmetric carbon atoms in the camphor nucleus, rigorous proof of the suggestion could not be obtained. It was proposed to confirm it by using an unsymmetrical β-diketone or β-ketonic ester which contained no asymmetric carbon atom and the basic or acidic group necessary for the resolution. *p*- and *m*-Aminobenzoylacetone and ethyl *p*-nitrobenzylacetoacetate appeared to fulfil these conditions. Owing to the resolution of beryllium benzoylpyruvate by Mills and Gotts (J., 1926, 3121), it was decided to place on record the results already obtained.

p-*Nitrobenzoylacetone.*—Freshly powdered sodamide (10·5 g.) was

slowly added to ethyl *p*-nitrobenzoate (50 g.) and acetone (19·8 c.c.) in dry ether (150 c.c.), cooled to −17°. The mixture immediately became greenish-black and ammonia was evolved. After being kept for 2 hours in the freezing mixture and for 20 hours at room temperature, the product was poured into ice-water, the ether separated, and the aqueous layer extracted twice with chloroform. (From these extractions, 16 g. of ethyl *p*-nitrobenzoate were recovered.) The aqueous layer was filtered through charcoal and acidified, and the resulting precipitate was filtered off and dried. This solid was extracted several times with ether, the ethereal solution was evaporated, and the resulting yellowish-brown crystals were recrystallised from methyl alcohol (yield, 1·5 g.), p-*nitrobenzoylacetone* being obtained in golden-yellow needles, m. p. 112—113·5° (Found: C, 58·1; H, 4·5; N, 6·8. $C_{10}H_9O_4N$ requires C, 57·95; H, 4·4; N, 6·8%). It is readily soluble in ordinary organic solvents except the cold alcohols and is insoluble in water. With caustic soda, it gives a bright yellow solution, and with copper acetate it produces a green precipitate, which is soluble in chloroform.

Beryllium p-*nitrobenzoylacetone* was obtained in nearly theoretical yield by the method described for beryllium benzoylcamphor (*loc. cit.*) (Found: C, 57·6*; H, 3·9*; Be, 2·2*. $C_{20}H_{16}O_8N_2Be$ requires C, 57·0; H, 3·8; Be, 2·1%). It is readily soluble in chloroform and hot benzene, from which it separates in brownish-yellow, compact crystals, m. p. 243—244°. It is sparingly soluble in alcohol and insoluble in water.

m-*Nitrobenzoylacetone*.—Preliminary experiments having shown that benzoylacetone can be recovered quantitatively from concentrated sulphuric acid at room temperature, the following nitration was carried out: A mixture of nitric acid (*d* 1·42; 7 c.c.) and sulphuric acid (*d* 1·84; 24 c.c.) was slowly added to benzoylacetone (15 g.) in sulphuric acid (100 c.c.), mechanically stirred and kept at −11° to −9°. After 15 minutes, the product was poured on ice; the precipitate obtained crystallised from hot methyl alcohol in very pale yellow needles, m. p. 114—115° (*p*-nitrobenzoylacetone depresses the m. p. by 20°) (yield, 47%) (Found: C, 58·1; H, 4·6%). m-*Nitrobenzoylacetone* is easily soluble in ordinary organic solvents except the cold alcohols and ligroin. The yellow coloration with alkalis is less intense than that of the *p*-nitro-derivative. With alcoholic ferric chloride, it gives a wine-red colour.

Beryllium m-*nitrobenzoylacetone*, prepared by the usual method, crystallised from acetone–alcohol in orange-yellow, square plates, m. p. 207—208° (Found: C, 57·3*; H, 3·9*; Be, 2·1%). It is

* Values so marked are the results of micro-estimations carried out by Siegmund Weil, Tübingen.

readily soluble in chloroform and benzene, less soluble in acetone, and slightly soluble in alcohol.

Ethyl Bis-p-*nitrobenzylacetoacetate.*—*p*-Nitrobenzyl bromide was slowly added to an equivalent quantity of ethyl sodioacetoacetate in absolute alcohol, sodium bromide being precipitated. After heating for 2 hours, the alcohol was evaporated, water added, and the precipitate crystallised from acetone–methylated spirit, *ethyl bis*-p-*nitrobenzylacetoacetate* separating in colourless flakes, m. p. 137—139° (Found: C, 60·5, 60·0; H, 5·0, 4·6; N, 6·8, 6·7. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0; N, 7·0%). It is readily soluble in acetone, ether, chloroform, and hot benzene, and sparingly soluble in cold alcohol. It gives a coloration neither with caustic soda nor with ferric chloride.

Ethyl p-*Nitrobenzylacetoacetate.*—The mother-liquor from the above compound left an orange-coloured oil on evaporation. This solidified when cooled in the ice-chest, and crystallised from benzene–ligroin in very pale yellow needles, m. p. 43—45° (Found: C, 59·05; H, 5·8. $C_{13}H_{15}O_5N$ requires C, 58·8; H, 5·7%). It is very soluble in all organic solvents except ligroin, in which it is sparingly soluble. With caustic soda, it gives an intense yellowish-orange coloration, and with ferric chloride a deep reddish-purple colour slowly develops. Copper acetate precipitates a green copper derivative, which is soluble in chloroform.

I wish to take this opportunity of expressing my thanks to the Chemical Society for a grant towards the expenses of the research, and also to Professor C. S. Gibson for his helpful criticism and encouragement.—Guy's Hospital Medical School. [*Received, March 21st*, 1927.]

The Reduction of Arsenic Compounds in Acid and in Alkaline Solution by Sodium Hyposulphite (Hydrosulphite). Production of Sodium Arseno-hyposulphite. By Walter Farmer and James Brierley Firth.

In an investigation on the reduction of certain arsenic compounds by sodium hyposulphite, in which a product corresponding to arsenic subsulphide, As_3S, was isolated (J., 1926, 119), it was inferred from preliminary experiments (and existing literature) that two intermediate complex compounds are formed, one of which is a decomposition product of the other.

The Primary Intermediate Complex, Sodium Arseno-hyposulphite, $Na_3As(S_2O_4)_3$.—Preliminary experiments carried out in glass vessels indicated that, in the presence of alcohol, shaking of an alkaline solution of trisodium arsenite containing hyposulphite was followed

by formation of two unstable precipitates, one of which was heavier than the other. Similar heavy precipitates were obtained when concentrated solutions of common sodium arsenate were used.

The products adhered to the walls of the vessel, and became viscous when treated with dilute alcoholic potash. In subsequent experiments, quartz containers were employed.

Sodium hyposulphite (2·75 g.) was introduced into a cold solution of 2·75 g. of common sodium arsenate in 3 c.c. of water to which a whirling motion had been imparted. The flask was closed, and the whirling maintained. Dissolution of the last traces of sodium hyposulphite was accompanied by formation of a heavy, granular solid, which settled in increasing quantity when the flask was kept at room temperature. The supernatant liquor was decanted off after 15 minutes, and the granular solid was washed five times by decantation with methylated alcohol and four times with benzene and kept in a quartz dish in a vacuum over sulphuric acid for 24 hours. A creamy-white powder was obtained (yield, 1 g.).

When a small quantity of the product was strongly heated in a Bunsen flame, a brown and a yellow sublimate formed and a garlic odour developed. If cautiously heated, the product first turned brown and, when more strongly heated, gave a brown and a yellow sublimate as before. When a small quantity of the product was treated with dilute hydrochloric acid, sulphur dioxide was evolved, and a brown product similar to that described in the previous paper (*loc. cit.*) formed.

Estimations of the arsenic content of the product, as magnesium pyroarsenate, gave: As, 14·1, 14·1, 14·1, 14·0%. Estimations of hyposulphite by Wilkes's method (*J. Soc. Chem. Ind.*, 1923, **42**, 356T) were based on the view that, in presence of hypoiodous acid, hydrolysis of 1 g.-mol. of arseno-hyposulphurous acid, $H_3As(S_2O_4)_3$, is attended by liberation of 4 g.-mols. of iodine according to the following equations:

(1) $H_3As(S_2O_4)_3 + 3H_2O = H_3AsO_3 + 3H_2S_2O_4$,
(2) $H_3AsO_3 + 2HIO + 3KOH = I_2 + K_3AsO_4 + 4H_2O$,
(3) $3H_2S_2O_4 + 9KIO + 6KOH = 6KHSO_4 + 9KI + 3H_2O$,
(4) $6KHSO_4 + 3KIO + 3KI = 3I_2 + 6K_2SO_4 + 3H_2O$.

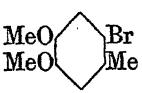
Two samples gave: S_2O_4, 70·9, 70·5 [$Na_3As(S_2O_4)_3$ requires As, 14·2; S_2O_4, 72·7%].

The Secondary Intermediate Complex, Sodium Arseno-thiosulphate, $Na_3As(S_2O_3)_3$.—Standard solutions of potassium hydroxide and hydrochloric acid of the same normality were prepared. 25 C.c. of the standard alkali in which 1 g. of sodium arseno-hyposulphite (1 mol.) and the calculated quantity of sodium sulphite (3 mols.)

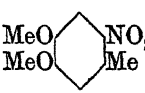
had been dissolved were rapidly added to 25 c.c. of the standard acid containing 2·5 c.c. of concentrated acid. A turbidity developed, followed by precipitation of arsenious sulphide. Decomposition of sodium arseno-hyposulphite in presence of sodium sulphite by this neutralisation method is considered to lead to formation, and rapid decomposition, of sodium arseno-thiosulphate, arsenious sulphide being one of the products (compare Jellinek, *Z. physikal. Chem.*, 1911, **76**, 257; Szilàgyi, *Z. anorg. Chem.*, 1920, **113**, 69).—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April 8th*, 1927.]

The Displacement of Bromine accompanying the Nitration of 6-Bromo homoveratrole. By TOM HEAP, THOMAS G. H. JONES, and ROBERT ROBINSON.

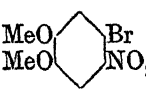
JONES and ROBINSON (J., 1917, **111**, 919) described the conversion of 6-bromohomoveratrole (I) into a mononitro-derivative, m. p. 121°, by the action of a mixture of nitric acid and acetic anhydride.



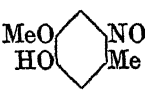
(I.)



(II.)



(III.)



(IV.)

We have, however, been unable to repeat the preparation of the nitro-derivative, since, on several occasions, following the description as closely as possible, the sole product of a sluggish reaction was 6-nitrohomoveratrole (II) (yield, 36%). Although it may be that some variation of the conditions is responsible for this divergence, we think it more likely that the observation of Jones and Robinson was erroneous as the result of contamination of the creosol employed with guaiacol and that the compound isolated was 4-bromo-5-nitroveratrole (III), m. p. 124° (or 121—122°, see below).

It is no longer necessary to employ beechwood tar as a source of creosol, since the pure phenol can be readily obtained from vanillin by Clemmensen's method.

6-Bromohomoveratrole (I).—The reduction of vanillin (100 g.) by means of amalgamated zinc and hydrochloric acid (Oberlin, *Arch. Pharm.*, 1925, **263**, 641) gave creosol (60 g.), b. p. 220—225°/760 mm., which was converted by known methods into homoveratrole, b. p. 218—220°, m. p. 22° (yield, 91%), and then into 6-bromohomoveratrole, b. p. 265—267°, m. p. 31° (yield, 94%). The latter crystallised in truncated octahedra, and, on oxidation with potassium permanganate and boiling dilute aqueous sodium hydroxide for 1½ hours, yielded 6-bromoveratric acid; this, alone or mixed with a specimen obtained by brominating methyl veratrate and hydrolys-

ing the product, melted at 183—184°. When treated with a mixture of acetic anhydride and nitric acid under the conditions prescribed by Jones and Robinson (*loc. cit.*), bromohomoveratrole (20 g.) gave 6-nitrohomoveratrole (8·5 g.), which crystallised in yellow needles from methyl alcohol; m. p. 117—119°, alone or mixed with an authentic specimen (Found: C, 55·0; H, 5·8. Calc. for $C_9H_{11}O_4N$: C, 54·8; H, 5·6%).

6-*Nitro*iso*creosol* (IV).—Cardwell and Robinson (J., 1915, **107**, 256) commented on the fact that 6-nitrohomoveratrole is not readily hydrolysed by alkalis. It is certainly less readily attacked than nitroveratrole, but by following the procedure of Pollecoff and Robinson (J., 1918, **113**, 647) for the preparation of 4-nitroguaiacol an almost theoretical yield of the nitro*iso*creosol was obtained in 73 hours. The substance crystallised from aqueous alcohol in slender, pale yellow needles, m. p. 168—170° (Found: C, 52·6; H, 4·6; N, 7·6. $C_8H_9O_4N$ requires C, 52·5; H, 4·9; N, 7·7%). The *acetyl* derivative crystallised from alcohol in colourless, elongated, hexagonal plates, m. p. 100—101°. On methylation the phenol yielded 6-nitrohomoveratrole, m. p. 117—119°. The conditions applicable for its further nitration to 2 : 6-dinitro*iso*creosol were not ascertained, since the action of nitric acid led to the production of soluble orange-red substances.

6-*Bromoveratric Acid*.—When methyl veratrate is brominated in cold acetic acid solution and the product crystallised, the yield of pure methyl 6-bromoveratrate, m. p. 88—89°, is not satisfactory, and Professor Smiles has suggested to us that methyl 2-bromoveratrate may be produced in the reaction. On treatment with cold nitric acid (*d* 1·42) pure 6-bromoveratric acid, m. p. 183—184°, gave a 50% yield of 4-bromo-5-nitroveratrole, m. p. 121—122°, whilst the crude product gave a 36% yield of this substance under identical conditions. 4-Bromo-5-nitroveratrole, prepared from bromoveratrole, had m. p. 121—122°, and a mixture with the specimen from 6-bromoveratric acid had the same m. p. The matter will be further investigated, our chief concern at the moment being to confirm the recorded m. p.'s of 6-bromoveratric acid and its methyl ester.—THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1927.]

CCLXVI.—*The Constitution of Certain Salts and Acids in Solution as determined by Observations of Critical Solution Temperatures.*

By SYDNEY RAYMOND CARTER and NORMAN JOSEPH LANE MEGSON.

DURING the course of investigations on the behaviour of sulphur dioxide towards certain salts in acid solutions, the occurrence of complex formation with hydrogen chloride was frequently suspected. Thus, ferric chloride exhibited a far greater tendency than ferrous chloride to combine with hydrogen chloride (J., 1924, **125**, 1886), whilst cupric chloride only appeared to do so at acid concentrations above 7*N* (J., 1925, **127**, 505). Recent work by one of us (this vol., p. 1918) has indicated pronounced combination between hydrogen chloride and mercuric chloride [see also Abegg, "Handbuch der anorganischen Chemie," 1905, II, (2), 641], whilst the reaction between hydrogen chloride and sulphur dioxide or selenium dioxide is much less marked and probably only evident in high concentrations of acid.

It appeared that a study of the mutual miscibilities of liquids, as developed by Pfeiffer (*Z. physikal. Chem.*, 1892, **9**, 444), Timmermanns (*ibid.*, 1907, **58**, 128), and Patterson and his collaborators (*J. Physical Chem.*, 1925, **29**, 295; J., 1925, **127**, 624, 2544; 1926, 2787, 2791) might afford independent confirmation of such complex formation. We wished, however, to work at higher concentrations, if possible, and therefore it was necessary to test the applicability of the method in such cases, since recorded work has hitherto been restricted to the more dilute solutions.

The elevation of the critical solution temperature (*C.S.T.*) of a known mixture produced by each substance was determined separately and then the elevation due to the mixture of the substance with hydrogen chloride was observed. Any decrease from the theoretical elevation was assumed (when not accounted for by other means) to be due to complex formation. Two systems were employed: (1) water and phenol, and (2) water and *iso*butyric acid. The latter system, having a low *C.S.T.*, allows a considerable elevation before the boiling point is reached, and consequently a wide range of concentrations. It also has the advantage that the end-point is more easily determinable than is the case with phenol.

EXPERIMENTAL.

The determination of the *C.S.T.* was carried out in a test-tube fitted with a thermometer and glass stirrer. The apparatus was closed and provision was made for leading in a current of nitrogen

if required. The temperature was controlled by a water-bath and the *C.S.T.* in the case of *iso*butyric acid was observed by the appearance or disappearance of turbidity, as judged with a constant illuminant behind the tube, whilst for phenol, the apparent disappearance of the thermometer bulb was employed, as recommended by Patterson. Readings obtained in this way were reproducible to $\pm 0{\cdot}02°$.

The *iso*butyric acid with water gave a *C.S.T.* of 18·07° over a range of 26·8—28·6% of acid. Since this value is low compared with some of the values in the literature, a small amount of impurity is evidently present, but as this is probably *n*-butyric acid it is not likely to affect the results which follow.

In these results, C is the *molecular* concentration of salt per 1000 g. of total mixture (*i.e.*, water, organic solvent, and solute); e is the elevation of the *C.S.T.* in degrees; and E is the molecular elevation, *i.e.*, $E = e/C$. Table I gives the values of e for given concentrations of the separate constituents in the *iso*butyric acid–water system, as read from smoothed curves.

TABLE I.

C	0·02.	0·04.	0·06.	0·08.	0·10.	0·12.	0·16.	0·20.	0·24.
SeO_2	0·52°	1·00°	1·48°	1·96°	2·40°	2·78°	3·56°	4·30°	5·08°
HCl	2·22	4·00	5·62	7·20	8·62	10·02	12·64	15·20	17·68
$CuCl_2$	5·40	10·28	14·90	19·14	23·00	26·98	33·90	40·22	46·48
$FeCl_2$	5·80	11·04	15·96	20·72	25·14	29·60	38·30	47·10	(55·90)
$FeCl_3$	5·25	10·96	17·60	23·96	30·08	35·76	45·50	(52·90)	—

C	0·30.	0·40.	0·50.	0·60.	0·70.	0·80.	0·90.	1·00.	1·10.
SeO_2	6·24°	8·24°	10·36°	12·80°	14·90°	17·22°	19·60°	21·96°	24·25°
HCl	21·18	26·20	31·50	36·30	40·80	45·10	49·04	52·78	56·20

If these values of e and C be plotted graphically, the curves, with the exception of that of selenium dioxide, deviate from straight lines, giving a curvature which is concave towards the concentration axis. This is in accordance with the decreased ionisation to be expected at the higher concentrations.

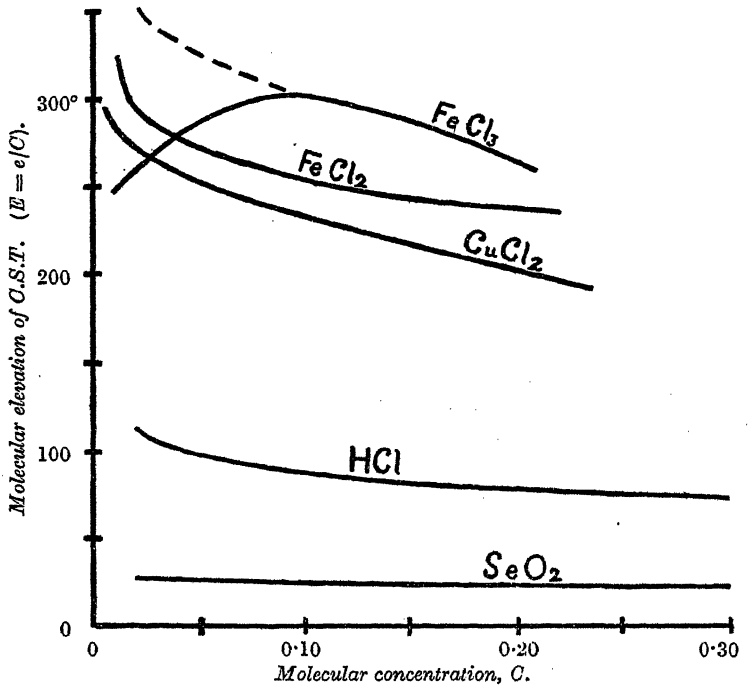
Ferric chloride gives a curvature near the origin which is slightly different from the remainder. These effects are much more clearly shown by plotting E against C (see Fig. 1).

For a normal substance such as hydrogen chloride, E increases with diminishing concentration as the result of ionisation. In the case of ferric chloride the increase ceases at $C = 0{\cdot}09$ and E falls rapidly with further dilution. Since hydrolysis begins to be appreciable at about the same stage, it probably affords an explanation (Goodwin, *Z. physikal. Chem.*, 1896, **21**, 15).

An interesting series of curves is obtained by plotting log e against log C. They approximate to parallel straight lines over a fair

range of concentration, the exception being that of ferric chloride, which crosses those of cupric and ferrous chlorides. The straight lines are in accordance with the equation $\log e = m \log C + b$, which gives the relation $e = AC^m$, proposed by Carrington, Hickson, and Patterson (J., 1925, **127**, 2548). The numerical value of the constant in our case gives $m = 0{\cdot}92$ for the system *iso*butyric acid–water, whilst the previous authors obtained $m = 0{\cdot}84$—$0{\cdot}87$ for phenol–water.

FIG. 1.



The regularity of the results obtained on plotting C against e and E, and $\log C$ against $\log e$, as well as of the results for the mixtures still to be described, suggests that the principles developed by Patterson in the more dilute solutions are also valid for the higher concentrations.

Mixtures of Salts with Hydrogen Chloride.

The possibility of complex formation was investigated, the concentration of the salt being kept approximately constant whilst that of the hydrogen chloride was varied over a fairly wide range. The theoretical elevation of the *C.S.T.*, denoted by "Mean e calc.,"

is half the sum of the elevations for *double* the concentration of each constituent, as described by Patterson (J., 1925, **127**, 626). This rule can be applied when the values of e for the salt and hydrogen chloride do not vary considerably, but for differences greater than 20° it is not so accurate.

TABLE II.

SeO_2 + HCl.					$CuCl_2$ + HCl.				
	C.	*e* calc.	Mean *e* calc.	*e* obs.		*C.*	*e* calc.	Mean *e* calc.	*e* obs.
SeO_2	0·681	30·58°	39·70°	39·63°	$CuCl_2$	0·103	41·20°	36·42°	36·75°
HCl	0·438	48·80			HCl	0·241	31·65		
SeO_2	0·347	14·78	26·66	27·87	$CuCl_2$	0·090	37·20	30·47	30·83
HCl	0·312	38·54			HCl	0·168	23·75		
$FeCl_2$ + HCl.									
$FeCl_2$	0·105	48·95	33·30	33·60	$FeCl_2$	0·0716	35·20	36·65	36·29
HCl	0·116	17·65			HCl	0·307	38·10		
$FeCl_2$	0·0703	34·60	31·20	31·08	$FeCl_2$	0·0681	33·80	26·49	26·47
HCl	0·205	27·80			HCl	0·128	19·81		

SO_2 + HCl.				
	C.	*e* calc.	Mean *e* calc.	*e* obs.
SO_2	(0·4)	5·0°	33·0°	34·2°
HCl	0·550	61·0		

No consistent lowering of e is thus observed for the mixtures SeO_2 + HCl, $FeCl_2$ + HCl, and $CuCl_2$ + HCl. The actual concentration of sulphur dioxide was not determined, since the same stock solution was used in making up both the SO_2 and the SO_2 + HCl mixtures for the determination of e. Only a slight increase in e is observed, and in view of the experimental errors involved, this may be interpreted as evidence of no combination between sulphur dioxide and hydrogen chloride at these concentrations.

Ferric Chloride and Hydrogen Chloride.—It was evident that some kind of reaction was taking place. When the ferric chloride alone was in the mixture of *iso*butyric acid and water, it imparted a dark brown colour to the organic layer. On addition of hydrogen chloride, this became lighter, assuming a light yellow colour when the ratio HCl : $FeCl_3$ reached 6 : 1. The concentration of ferric chloride was kept at *ca.* 0·08 whilst that of hydrogen chloride was varied from 0·08 to 0·50, and in these circumstances depressions of e were observed as shown in Table III.

The consistent appreciable decrease in e is evidence of complex formation, and since the greatest percentage decrease occurs when HCl : $FeCl_3$ = 3 : 1, it appears probable that the compound $FeCl_3$,3HCl exists in solution.

The complex ferric compounds which are formed by carboxylic

TABLE III.

C.		*e* calc.					
$FeCl_3$.	HCl.	$FeCl_3$.	HCl.	Mean *e* calc.	*e* obs.	Diff.	Decrease in *e*, %.
0·0766	0·0790	43·65°	13·00°	28·33°	29·36°	+1·03°	—
0·0824	0·1715	46·42	27·40	34·91	33·33	−1·58	4·6
0·0836	0·2446	46·80	31·42	39·11	36·63	−2·48	6·5
0·0844	0·2625	47·20	32·72	39·96	37·08	−2·88	7·5
0·0869	0·2770	48·20	34·10	41·15	37·98	−3·17	8·0
0·0815	0·3145	46·10	37·65	41·87	39·77	−2·10	5·1
0·0764	0·4370	44·00	48·10	46·05	43·51	−2·54	5·7

acids, such as acetic acid, might be expected to explain the anomalous behaviour of ferric chloride in *iso*butyric acid:

$3FeCl_3 + 6CH_3{\cdot}CO_2H + 2H_2O \rightleftharpoons [Fe_3(OH)_2(CH_3{\cdot}CO_2{\cdot})_6]Cl + 8HCl$

(Weinland, " Complex-Verbindungen," 1919, pp. 345 *et seq.*). The brown coloration may then be satisfactorily attributed to the coloured complex, whilst the subsequent addition of hydrochloric acid leads to the repression of complex formation and a consequent fading of colour.

The occurrence of complex formation causes solubility of the ferric chloride in both liquids instead of in the water alone, and this would tend to decrease the *C.S.T.*, especially for higher concentrations of ferric chloride. Since, however, the abnormalities in *C.S.T.* are mainly observed at the lower concentrations of ferric chloride, and in the opposite sense, we consider that the extent of interaction between the ferric chloride and *iso*butyric acid must be relatively small.

For the remaining examples, the phenol–water system was found more convenient.

Mercuric Chloride and Hydrogen Chloride.—Mercuric chloride is soluble both in phenol and in *iso*butyric acid, but the former solvent was found to be more suitable to work with. The *C.S.T.* was depressed and *e* was negative (Table IV).

TABLE IV.

C	0·05	0·10	0·15	0·20	0·25
$-e$ for $HgCl_2$	1·72°	3·58°	5·58°	7·72°	9·85°
$+e$ for HCl.....	3·58	6·50	9·02	11·38	13·60
C	0·30	0·35	0·40	0·50	0·60
$-e$ for $HgCl_2$	12·00°	14·10°	—	—	—
$+e$ for HCl.....	15·80	17·50	19·18	22·20	(24·7)

The graph of log *C* against log *e* for mercuric chloride is a straight line and its slope indicates $m = 1{\cdot}1$. This differs from the normal value, 0·87, for ordinary substances insoluble in phenol.

The concentration of mercuric chloride was kept nearly constant and that of hydrogen chloride varied; the results obtained are given in Table V, and afford an example of the *C.S.T.* being raised by a

TABLE V.

C_{HgCl_2}.	C_{HCl}.	Mean e calc.	e obs.	Increase.
0·248	0·108	−4·2°	− 3·5°	0·7°
0·243	0·168	−1·5	+ 0·1	1·6
0·245	0·250	+1·05	+ 4·79	3·74
0·249	0·278	+1·55	+ 6·81	5·26
0·244	0·456	+6·20	+15·20	9·0
0·244	0·479	+6·65	+15·84	9·2
0·226	0·595	+9·75	+21·66	11·9

mixture. It is raised to an extent greater than would be expected from the simple mixture, and the effect increases with relative increase in the ratio $HCl/HgCl_2$. Since one of the constituents, mercuric chloride, is soluble in the phenol layer, it shows that a complex is being formed which is insoluble in phenol.

Cuprous Chloride and Hydrogen Chloride.—The value "Mean e calc." = (25°) is an approximation and indicates a lower limit, since "e calc." has been estimated by analogy with the chlorides of univalent metals. If cuprous copper exerts a higher valency as in the double formula Cu_2Cl_2 a still higher value would result. In either case, the low value of e obs. is thus in accordance with complex formation.

(Phenol–water system.)

	C.	e calc.	Mean e calc.	e obs.
HCl	0·422	35°	(25°)	22·2°
CuCl	0·0836	(15)		

Summary.

The elevation of critical solution temperature has been employed in order to study complex formation in hydrogen chloride solutions.

The values of e for various salts and acids have been determined in the system *iso*butyric acid–water, and for mercuric chloride in the phenol–water system.

Values of e and E obtained for these salts are regular, except in the case of ferric chloride, in which hydrolysis probably occurs.

The constant m approximates to 0·92 in the equation $e = AC^m$ for *iso*butyric acid–water.

No complex formation has been found between hydrogen chloride and sulphur dioxide, selenium dioxide, or ferrous and cupric chlorides, but considerable complex formation occurs between hydrogen chloride and ferric, mercuric, or cuprous chloride in the concentrations used.

The concentrations are considerably higher than those used hitherto, but the principles are still applicable.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, February 19th*, 1927.]

CCLXVII.—*The Electronic Structure of Atoms. Part I. The Periodic Classification.*

By J. D. Main Smith.

The outstanding feature of theories of the structure of atoms is their extensive and intimate relationship to the facts of chemistry summarised in the periodic classification of the elements. This relationship consists essentially in referring the periodicity in the properties of elements to a corresponding periodicity in the structural complexity of their atoms. The existence of this correspondence is readily deducible from a multitude of correlated chemical and physical experimental facts, but its precise nature has been variously interpreted, and diverging views have consequently been held as to the electronic structures attributable to the atoms of the elements.

Examination of the arrangement of the elements in the order of atomic weight shows that characteristic types of elements recur at fixed intervals or periods. The number of elements intervening in a period is always 8, 18, or 32. For example, if the noble gases be taken as points of reference, there are 8 elements from helium to neon and from neon to argon, 18 from argon to krypton and from krypton to xenon, and 32 from xenon to radon.

These sets of elements constitute Mendeléev's periods (see Table 1), the first two sets of 8 elements forming the first two "short"

Table 1.

Periodic Classification.

Group. Valency.	I. +1	II. +2	III. +3	IV. +4 −4	V. +5 −3	VI. +6 −2	VII. +7 −1	VIII. Zero or +8
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K 29Cu	20Ca 30Zn	21Sc 31Ga	22Ti 32Ge	23V 33As	24Cr 34Se	25Mn 35Br	26Fe,27Co,28Ni,(Cu,Zn) 36Kr
5	37Rb 47Ag	38Sr 48Cd	39Y 49In	40Zr 50Sn	41Cb 51Sb	42Mo 52Te	43Ma 53I	44Ru,45Rh,46Pd,(Ag,Cd) 54Xe
6	55Cs 79Au	56Ba 80Hg	57La+ * 14 "Rare Earths" 81Tl	72Ct 82Pb	73Ta 83Bi	74W 84Po	75Re 85—	76Os,77Ir,78Pt,(Au,Hg) 86Rn
7	87—	88Ra	89Ac	90Th	91Pa	92U		

* 58Ce, 59Pr, 60Nd, 61Il, 62Sm, 63Eu, 64Gd, 65Tb, 66Dy, 67Ho, 68Er, 69Tm, 70Yb, 71Lu

periods, and the remaining sets of more than eight elements forming the "long" periods. The first two long periods of 18 elements fall into two series of eight valency groups, the "even" series consisting of 10 elements (three in Group VIII), and the "odd"

series of 8 elements. The third long period, containing 32 elements, has been a subject of much discussion, but it is now generally agreed that it is divisible into two series or sub-periods like the other long periods, the even series, however, being of 24 elements, from cæsium to platinum, and the odd series as before of eight elements, from gold to the noble gas radon. It is assumed that in this period only one element, eka-iodine, belonging to the halogen group, remains to be discovered.

The Abridged Periodic Classification.

The history of chemical science has demonstrated clearly that the most useful method for the condensation and generalisation of data is that of classification by types. In organic chemistry, the method proceeds according to constitutional types, such as alcohols, ketones, aldehydes, etc., by reference to *structural* features possessed in common by *compounds*. In inorganic and general chemistry, the method proceeds similarly according to constitutional types, by reference to *valency* features possessed in common by *atoms*. The periodic classification is essentially classification by valency types, the elements being arranged into eight groups having valency from one to eight respectively. This supremely important octet classification is somewhat obscured by the detail introduced by the division of the long periods into the unequal sub-periods of the even and odd series. Modifications intended to simplify and increase the chemical utility of the classification must emphasise this octet arrangement. Many of those proposed in recent years, however, have had for their object, not the increase in the chemical utility of classification of detailed knowledge, but the facilitation of mathematical interpretations of atomic structure, and with this in view the number of groups is successively increased from 8 to 18 and 32 in passing from the short to the long periods. In all such systems, the essential chemical features of classification by valency and periodicity of properties are subordinated or suppressed, although the structure of atoms is fundamentally a chemical problem, profoundly interwoven with the periodic classification of the elements. It will be shown that abridgment, rather than expansion, clarifies the classification, and facilitates a more intimate and accurate interpretation of atomic structures, by throwing the chemically important octet arrangement into high relief.

In the classification of the elements by valency types, the 16 light elements from lithium to argon fall naturally into two periods of eight groups with one element per group per period, each period ending with a noble gas. These two periods may, consequently, be regarded as simple or specific types for the heavier elements of

the long periods. Consideration of the properties of these heavier elements shows that, in each long period, only a few elements approximate closely in properties to the simple types of the short

TABLE 2.

Abridged Periodic Classification.

Class.	Alkaline.		Amphoteric.		Non-Basic.			
Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Valency.	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	Zero
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K	20Ca*	31Ga	32Ge	33As	34Se	35Br	36Kr
5	37Rb	38Sr†	49In	50Sn	51Sb	52Te	53I	54Xe
6	55Cs	56Ba‡	81Tl	82Pb	83Bi	84Po	85—	86Rn
7	87—	88Ra§						

* 10 Elements, 21Sc to 30Zn
† 10 Elements, 39Y to 48Cd
‡ 24 Elements, 57La to 80Hg
§ All elements from 89Ac
} relegated to Table 3.

periods, and that in any one period some of these kindred elements appear in the even and some in the odd series. Mendeléev suggested that the elements diverging most from the specific types were in the nature of " transition " elements bridging a gap between the typical elements of each long period, a view adopted later in a modified form by Bohr in his theory of atomic structure. Mendeléev's suggestion is virtually a recognition that the long periods can be short-circuited by excluding the transition elements, leaving an abridged classification constituted solely of elements closely related to the short period types, the periodic classification thus consisting only of simple periods each of eight elements.

In order to effect this short-circuiting or abridgment of the long periods, it is necessary to decide which elements are most closely related to the typical elements of the short periods, the remaining elements being relegated to transition series. In the first long period (see Table 1), it is evident that potassium and the elements from gallium to krypton are more closely related to sodium and the elements from aluminium to argon than are copper and the elements from scandium to nickel, and these last nine elements are therefore definitely transition elements. There remain only calcium and zinc for consideration. As one of the obvious features of the periodic classification is the increase in basicity with increase in atomic weight in each group, the element corresponding to magnesium, the oxide of which is feebly alkaline, should possess a strongly alkaline oxide, the heavier members of the group having still more alkaline

series of 8 elements. The third long period, containing 32 elements, has been a subject of much discussion, but it is now generally agreed that it is divisible into two series or sub-periods like the other long periods, the even series, however, being of 24 elements, from cæsium to platinum, and the odd series as before of eight elements, from gold to the noble gas radon. It is assumed that in this period only one element, eka-iodine, belonging to the halogen group, remains to be discovered.

The Abridged Periodic Classification.

The history of chemical science has demonstrated clearly that the most useful method for the condensation and generalisation of data is that of classification by types. In organic chemistry, the method proceeds according to constitutional types, such as alcohols, ketones, aldehydes, etc., by reference to *structural* features possessed in common by *compounds*. In inorganic and general chemistry, the method proceeds similarly according to constitutional types, by reference to *valency* features possessed in common by *atoms*. The periodic classification is essentially classification by valency types, the elements being arranged into eight groups having valency from one to eight respectively. This supremely important octet classification is somewhat obscured by the detail introduced by the division of the long periods into the unequal sub-periods of the even and odd series. Modifications intended to simplify and increase the chemical utility of the classification must emphasise this octet arrangement. Many of those proposed in recent years, however, have had for their object, not the increase in the chemical utility of classification of detailed knowledge, but the facilitation of mathematical interpretations of atomic structure, and with this in view the number of groups is successively increased from 8 to 18 and 32 in passing from the short to the long periods. In all such systems, the essential chemical features of classification by valency and periodicity of properties are subordinated or suppressed, although the structure of atoms is fundamentally a chemical problem, profoundly interwoven with the periodic classification of the elements. It will be shown that abridgment, rather than expansion, clarifies the classification, and facilitates a more intimate and accurate interpretation of atomic structures, by throwing the chemically important octet arrangement into high relief.

In the classification of the elements by valency types, the 16 light elements from lithium to argon fall naturally into two periods of eight groups with one element per group per period, each period ending with a noble gas. These two periods may, consequently, be regarded as simple or specific types for the heavier elements of

the long periods. Consideration of the properties of these heavier elements shows that, in each long period, only a few elements approximate closely in properties to the simple types of the short

TABLE 2.

Abridged Periodic Classification.

Class.	Alkaline.		Amphoteric.		Non-Basic.			
Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Valency.	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	Zero
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K	20Ca*	31Ga	32Ge	33As	34Se	35Br	36Kr
5	37Rb	38Sr†	49In	50Sn	51Sb	52Te	53I	54Xe
6	55Cs	56Ba‡	81Tl	82Pb	83Bi	84Po	85—	86Rn
7	87—	88Ra§						

* 10 Elements, 21Sc to 30Zn
† 10 Elements, 39Y to 48Cd
‡ 24 Elements, 57La to 80Hg
§ All elements from 89Ac
} relegated to Table 3.

periods, and that in any one period some of these kindred elements appear in the even and some in the odd series. Mendeléev suggested that the elements diverging most from the specific types were in the nature of " transition " elements bridging a gap between the typical elements of each long period, a view adopted later in a modified form by Bohr in his theory of atomic structure. Mendeléev's suggestion is virtually a recognition that the long periods can be short-circuited by excluding the transition elements, leaving an abridged classification constituted solely of elements closely related to the short period types, the periodic classification thus consisting only of simple periods each of eight elements.

In order to effect this short-circuiting or abridgment of the long periods, it is necessary to decide which elements are most closely related to the typical elements of the short periods, the remaining elements being relegated to transition series. In the first long period (see Table 1), it is evident that potassium and the elements from gallium to krypton are more closely related to sodium and the elements from aluminium to argon than are copper and the elements from scandium to nickel, and these last nine elements are therefore definitely transition elements. There remain only calcium and zinc for consideration. As one of the obvious features of the periodic classification is the increase in basicity with increase in atomic weight in each group, the element corresponding to magnesium, the oxide of which is feebly alkaline, should possess a strongly alkaline oxide, the heavier members of the group having still more alkaline

oxides. This circumstance involves that the congeners of beryllium and magnesium are the alkaline-earth metals, calcium, strontium, barium and radium, whilst zinc, cadmium, and mercury are transition elements.

The transition elements of the first long period are consequently the ten elements from scandium to zinc (see Table 3). The remaining eight elements, potassium, calcium, and gallium to krypton, form an abridged period (see Table 2) with one element per periodic group, exhibiting extremely close resemblance to the typical elements of the short periods. Similar considerations apply to the second long period, the transition elements being the ten from yttrium to cadmium (see Table 3). The remaining eight elements, rubidium, strontium, and indium to xenon, form an abridged period with one element per periodic group. In the third long period, consisting of 32 elements, it is similarly possible to allocate the eight elements cæsium, barium, and thallium to radon to the abridged period. The 24 elements from lanthanum to mercury are in consequence relegated to the transition series.

In the fourth long period, the known elements come to an end with uranium in Group VI of the even series. The chemical and physical properties of actinium, thorium, protactinium, and uranium indicate decisively that they are analogues of yttrium, zirconium, etc., and therefore transition elements. The only remaining known element of the period is radium, which resembles barium so closely that it can be separated from it only with difficulty. Radium consequently is an alkaline-earth metal and must be regarded, not as a transition element, but as the Group II representative in the abridged classification. Similarly, eka-cæsium must, as an alkali metal, be postulated as the Group I representative of the abridged classification, not as a transition element. The existence of only one element, actinium, between thorium and radium renders it certain that the transition series of this last long period contains no transition sub-series similar to the anomalous 14 "rare-earth" elements (see p. 2035), and it is consequently probable that, if all the elements of this period were known, they would number only 18 as in the case of the first and second long periods.

There remain for consideration only the two lightest elements, hydrogen and helium. Apart from hydrogen, no element lighter than helium is known, and many considerations, chemical and physical, render it improbable that any other element can exist. If it be admitted that electrons are the sole valency factors, the fact that helium contains only two electrons makes it certain that hydrogen with one electron is the only possible element lighter than helium. Despite the validity and utility of the octet classification,

it is thus impossible to fill more than two of the eight groups of this primitive period. As the unit of valency and of atomic weight, hydrogen may be regarded as the type of all the valent elements and placed at the head of any of the Groups I to VII of the classification, helium being placed at the head of Group VIII as the type of all the non-valent and noble elements. It is not a matter of importance, in the classification of the elements, in which group hydrogen is placed, but from its univalency it may conveniently be placed in Group I *and* alternatively in Group VII.

The modification of the periodic classification derived from the foregoing considerations is shown in Table 2, and consists of a primitive period of two elements, two short periods each of eight elements, three abridged long periods each of eight elements, and a final abridged and incomplete period, or seven periods in all. Examination of these seven abridged periods reveals much greater regularities in the classification than are readily discernible in the extended form. Basicity, for example, *diminishes* regularly in each *period* from strong alkalinity in the first group to strong acidity in the seventh, and *increases* regularly in each *group* from the first to the seventh period. Further, all the elements which possess alkaline oxides are confined to Groups I and II. The alkaline thallous and plumbous oxides are only apparent exceptions to this rule, for in neither case does the metal exhibit the valency characteristic of the periodic group to which it belongs. This disappearance of alkalinity beyond Group II is of fundamental importance in the interpretation of the electronic structures of the atoms of all the elements, in Groups III to VIII no less than in Groups I and II, for, being a measure of electron mobility, it enables a differentiation to be made amongst the various sub-groups of electrons that constitute the exterior of atoms.

Comparison of Groups III and IV with Groups V, VI, and VII brings to light a further regularity relating to basicity. The whole of the elements of Groups III and IV possess amphoteric oxides, their basic tendencies being approximately equal to their acidic tendencies, and, where the elements exhibit lower valency, the lower oxides are never amphoteric but decidedly basic or even alkaline, as in the case of thallous and plumbous oxides. In Groups V to VIII, on the other hand, all the elements yield oxides which are strongly acidic, and, even where the basic properties are in any degree exhibited by the oxides, as in the case of bismuth and antimony, the derived salts are without exception hydrolysed by water to basic salts. Further, where the elements of Groups V to VII exhibit lower valency than that characteristic of the group, even the lower oxides are usually strongly acidic. Groups V to

VIII, moreover, include every known element which is gaseous below a red heat. The elements of Groups III and IV are consequently as sharply differentiated from those of Groups V to VII as from those of Groups I and II. The periodic classification can thus be divided, not only into groups, periods, and even, odd, and transition series, but also into classes of groups; the first class, Groups I and II, contains what may be termed the alkaline elements; the second class, Groups III and IV, the amphoteric elements; and the third class, Groups V, VI, VII, and VIII, the non-basic elements.

Variable Valency.

A further noteworthy feature of the abridged classification is that, without exception, every element exhibiting variable valency possesses valencies which differ by only 2, 4, or 6 units, iodine, for example, having valencies of 7, 5, 3, and 1. Apparent exceptions to this rule may be found in the case of gallium and indium : both metals, though normally tervalent, are stated to yield bivalent salts, while indium is stated to yield univalent salts in addition. The vapour density of indium " dichloride " slightly above its boiling point, however, proves the formula to be In_2Cl_4, not $InCl_2$. The dichloride has therefore no real existence, and it may be regarded as a double salt of the monochloride and trichloride, $InCl,InCl_3$ or $In(InCl_4)$. Gallium " dichloride " boils at 535°, but its vapour density has been recorded only at 1000° where it is normal. If, however, the formula is Ga_2Cl_4 and dissociation occurs on heating to a mixture of GaCl and $GaCl_3$, the vapour density of the mixture will be the same as that of $GaCl_2$. Fused gallium trichloride is a non-electrolyte, like aluminium chloride, whereas the alleged dichloride is a good conductor and readily yields metallic gallium on electrolysis, pointing to the formula $Ga(GaCl_4)$ or Ga_2Cl_4. A similar dimeric " dichloride " is obtained from thallium by mixing the monochloride with the trichloride, and it is definitely known that thallium does not exhibit bivalency. If gallium and indium " dichlorides " are, as suggested, really gallous gallichloride and indous indichloride, respectively, these two metals fall into line with thallium in the same group as possessing only tervalency and univalency, and the apparent exceptions to the rule of variation by two units of valency disappear from the abridged classification.

The Transition Series.

It has been shown, in connexion with the abridgment of the periodic classification, that 10 elements in each of the first two long periods, 24 in the third long period, and four of the six known elements of the last period show very considerable divergence from

the properties of the typical elements of the two short periods, and are to be regarded as transition elements bridging a gap in each long period between elements most closely allied to the typical elements. In the first long period, these ten transition elements, from scandium to zinc, may be arranged in a sub-period or transition series consisting, like the abridged periods, of eight valency groups (see Table 3). The lightest member of the series, scandium, with an

TABLE 3.

All Transition Series.

Group.	III.	IV.	V.	VI.	VII.	VIII.			I.	II.
Valency.	+3 to 2	+4 to 2	+5 to 2	+6 to 2	+7 to 2	+8 to Zero			+1 to 3	+2 to 1
Period.										
4	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn
5	39Y	40Zr	41Ob	42Mo	43Ma	44Ru	45Rh	46Pd	47Ag	48Cd
6	57La*	72Ot	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg
7	89Ac	90Th	91Pa	92U						

* 14 Elements, 58Ce to 71Lu, relegated to Table 4.

invariable valency of three, naturally falls into Group III, the heaviest member, zinc, with an invariable valency of two, being proper to Group II, the transition period thus commencing with Group III and ending with Group II.

The set of ten transition elements from the second long period correspond so closely in chemical and physical properties to the ten transition elements from the first long period that, without further discussion, they may be allocated to the corresponding eight groups from III to II (see Table 3).

Owing to the fact that there are 24 transition elements in the third long period as against 10 in the other two long periods, no complete analogy exists, but the nine elements from celtium (hafnium) to mercury in this longest transition series present so close a resemblance to the nine elements in the preceding transition series, from zirconium to cadmium, that they may readily be allocated to the seven corresponding periodic groups from IV to II. There remain in this transition series only the 15 elements having atomic weights lying between barium in Group II and celtium (hafnium) in Group IV. These elements from lanthanum to lutecium (known as " rare-earth " elements) have characteristic tervalency, are relatively strong bases, and give rise to basic salts of the type $La(OH)CO_3$, and mixed salts of the type $LaFCO_3$. There can, therefore, be no doubt that these elements are completely analogous to yttrium and scandium, and are proper to Group III. This transition series of 24 elements may be short-circuited or abridged (see Table 3) by the omission of 14 of the 15 " rare-earth " elements in Group III, leaving an abridged transition series of 10

elements corresponding closely in every member to each of the transition series from the first two long periods. It is not a matter of great importance chemically which 14 "rare-earth" elements are relegated to a transition sub-series, but the relegation is of prime importance in the problem of the electronic structures of the atoms of this period. It is consequently necessary to make a decision, on chemical grounds if possible, as to the element presenting the closest resemblance to yttrium and scandium in the two preceding transition series, and to place the other fourteen in a transition sub-series. Scandium and yttrium have no valency higher than three, whilst yttrium (certainly) and scandium (probably) exhibit the valency of two in acetylenic carbides of the form YC_2. Both yield colourless, diamagnetic salts, while yttrium oxide is a stronger base than scandium oxide, the basicity of the former only just falling short of alkalinity. Consequently the element to be placed in Group III of the third transition series should have no higher valency than three, exhibit a valency of two in an acetylenic carbide, and possess colourless, diamagnetic salts and a strongly alkaline oxide. These properties are possessed only by the lightest of these elements, lanthanum, which must, accordingly, be regarded as the Group III representative in the transition series of the third long period, the remaining 14 from cerium to lutecium, being relegated to a transition sub-series (see Table 4). This transition sub-series

TABLE 4.

Transition Sub-series, Period 6.

Element.	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Valency.	2	2	2		2	2				2			2	
	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4					4						

presents no analogy to the transition sub-period or to the main period, for these are real periods consisting of eight groups, whereas the elements of the transition sub-series do not exhibit valency less than two or greater than four, and thus cannot form a period. From time to time it has been proposed to place cerium in Group IV on the grounds of its quadrivalency and the isomorphism of some few of its salts with those of thorium and zirconium. These proposals have lost much of their point since the discovery of celtium (hafnium), properly allocated to Group IV because of its extraordinarily close resemblance to zirconium. It will, moreover, be shown, in discussing the electronic structure of atoms, that the allocation of cerium to Group III and to the transition sub-series on chemical grounds is fully justified, in that the electron responsible

for the increase in the valency of cerium from three to four is probably structurally unrelated to any of the electrons responsible for the quadrivalency of celtium (hafnium) or indeed of any element in either the main or transition periods.

The transition sub-periods (Table 3), based upon the foregoing considerations, comprise two typical periods each of ten elements, an abridged period also of ten elements, and a final incomplete period, all the periods commencing with Group III and ending with Group II.

With the possible exceptions of scandium and zinc (although scandium possesses an acetylenic carbide of the probable formula ScC_2, in which the metal would be bivalent), all the transition elements exhibit variable valency, and this variation can and usually does occur by one unit, instead of by the invariable two units of the abridged classification. With very few exceptions, the transition elements give rise to coloured salts, whereas the elements of the abridged classification form only colourless salts. Unlike the abridged periodic classification, the groups of which are divisible into a class of two alkaline groups, a second class of two amphoteric groups, and a third class of four non-basic groups, the transition classification consists of only one strongly basic group, III, the other seven groups almost without exception comprising only elements with either amphoteric or strongly acidic properties in their highest oxides, although the acidic properties are feeble in Groups I and II.

The Complete Periodic Classification.

On recombining the transition classification (Table 3) with the abridged classification (Table 2), the full periodic classification including the whole of the elements is obtained (Table 1). This table differs from the commonly accepted forms in small but important features. Seven main periods suffice to include all the known elements, a primitive period of two elements, two simple periods each of eight elements, and four complex periods consisting each of two sub-periods. Each period comprises only eight groups, commencing with Group I and ending with Group VIII, the simple periods and the main sub-periods of the long periods terminating with noble gases and the transition sub-periods with noble metals. In order to indicate their close resemblance to the noble metals of Group VIII, the pairs copper and zinc, silver and cadmium, and gold and mercury, are alternatively included also in this group, just as hydrogen is alternatively included in Group VII to indicate its resemblance to the halogen elements.

The transition elements in each long period are shown in heavy type, the arrows between elements of Groups II and III indicating

the position at which the transition elements create a gap between the typical elements of the periods. In order to preserve the symmetry of the octet classification, the 15 rare-earth elements, belonging to Group III and succeeding barium in atomic weight, are represented only by their most typical member, lanthanum, the other 14 being shown in detail in a footnote to the table. In order to facilitate the identification of the typical members of each group, which constitute the abridged classification, they are placed to the left and the transition elements to the right of the columns.

The abridged classification, the transition classification, the transition sub-series, and the complete periodic classification, shown in Tables 1, 2, 3, and 4, respectively, together with the experimental chemical evidence on which they are founded, will form the basis of subsequent papers on the interpretation of chemical evidence in terms of the distribution of electrons in atomic structures. The next paper will show primarily that the octet classification is due to the existence of from one to eight outer electrons in three sub-groups completed to 2, 2, 4 in the inert gases; that the transition classification is due to from one to eight more deeply seated electrons in two sub-groups completed to 4, 6 and forming part of a main group in five sub-groups of 2, 2, 4, 4, 6, completed in Group I; and that the transition sub-series is due to from one to fourteen still more deeply seated electrons completed to 6, 8, and forming part of a main group in seven sub-groups of 2, 2, 4, 4, 6, 6, 8, completed in lutecium. This scheme of atomic structure was first put forward by the author on incomplete evidence on March 9th, 1924 (*J. Soc. Chem. Ind.*, **43**, 323), and is now found to be fully justified in the light of additional evidence chiefly furnished by the foregoing periodic classifications.

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THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCLXVIII.—*Molecular Structure in Solution. Part II. The Refractive Indices and Surface Tensions of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid.*

By Owen Rhys Howell.

The densities and viscosities of a series of solutions having a fixed concentration of cobalt but increasing concentrations of hydrochloric acid, and also those of an exactly similar series of solutions of the acid alone, have already been determined (this vol., p. 158). It was shown that the differences in the densities of corresponding solutions varied with increasing concentration of acid, the curve exhibiting a point of inflexion. The differences in the viscosities of corresponding solutions also varied, the curve showing a well-defined maximum. The point of inflexion in the one case and the maximum in the other occurred at precisely the same concentration of acid.

The work of Hill and Howell (*Phil. Mag.*, 1924, **48**, 833) suggests that in the red pigments and solutions the cobaltous atom is surrounded by six other atoms or groups, whilst in the blue pigments and solutions it is surrounded by four, and the results outlined above were interpreted by assuming that with increasing concentration of acid, the cobalt atom is thrown out of its association with six molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, into one with four atoms of chlorine, $CoCl_4''$. It was deemed of interest to determine other physical properties of these solutions in order to ascertain whether they also would show similar variations; the refractive indices and surface tensions have therefore been measured.

Experimental.

Determination of Refractive Index.—The measurements were made with a Pulfrich refractometer. In order that the results should be directly comparable with those already obtained for the densities and viscosities, all determinations were made at 20°.

Since all the solutions were acidic, it was impossible to utilise the usual attachment for temperature regulation. The whole instrument was therefore encased by means of asbestos mill-board cut to shape, and the temperature was kept constant to within ± 0·5° by regulating a small gas flame placed inside the case. The cell was covered with a watch-glass to prevent loss of acid.

Measurements were made for the D line with a sodium flame, and for the C, F, and G′ lines with a hydrogen tube. The refractive index of every solution in the series containing acid only was deter-

mined for each of these lines, but this was impossible with the series containing cobalt since these solutions are coloured. Although the red solutions have strong absorption bands in the blue region, with the concentration of cobalt taken the F and G′ lines were transmitted sufficiently well to enable measurements to be made. The refractive index for each of these two lines has therefore been determined for every member of the series of solutions containing cobalt. The blue solutions, however, are much more intense than the red, and with these the C and D lines were completely extinguished. It was therefore possible to determine the refractive index for these two lines only with the solutions at the red end of the series.

Readings could be reproduced to within 1′ even with the faintest lines and to within 0·5′ with strong ones. The values of the refractive index are therefore all correct to the fourth place of decimals and most of them to within 5 units in the fifth place.

Determination of Surface Tension.—The measurements were made with a Traube stalagmometer. The lower capillary and also a long open tube were passed through a rubber stopper fitted into a small bottle. The stalagmometer was filled with the solution, and a little of this was also placed in the bottle in order to saturate with the vapour the atmosphere in which the drops formed. The apparatus was immersed vertically (against a plumb-line) in a glass-fronted thermostat kept at 20° ± 0·01°. The surface tension was calculated from the formula

$$\gamma_{\text{sol.}} = \gamma_{\text{water}} \times n_w/n_s \times d_s,$$

where n_w and n_s are the number of drops given by water and by the solution respectively, and d_s is the relative density of the solution. The value $\gamma_{20°} = 72{\cdot}69$ for water was employed, and the values of the relative density used were those determined in the previous investigation.

It has been shown (Lohnstein, *Z. physikal. Chem.*, 1908, **64**, 686; 1913, **84**, 410; Harkins and Humphery, *J. Amer. Chem. Soc.*, 1916, **38**, 228; Harkins and Brown, *ibid.*, 1919, **41**, 499) that the simple formula for the surface tension requires a correction factor depending on the ratio of the radius of the tip to the linear dimensions of the drop. If r is the radius of the tip and v the volume of the drop, then when $r/v^{\frac{1}{3}}$ lies between 0·76 and 0·95 the correction is practically constant. In a comparative method of determining surface tension the correction factor would then cancel, leaving the equation given above as a true expression.

The diameter of the tip of the stalagmometer used for these experiments was 0·87 cm. The volumes of the largest drops (given

by water) and of the smallest (given by the most concentrated acid solution) were determined by weighing and found to be 0·1268 c.c. and 0·1021 c.c., respectively. The extreme values of the ratio r/v are therefore 0·865 and 0·930. Since these fall within the limits for the constancy of the correction factor, the simple equation used for the calculation is sufficiently accurate.

With the solution yielding the smallest drops, each drop corresponded to 18 divisions on the scale. Since the determinations could be reproduced to within 0·5—1·0 division, the measurements are correct to within about $\pm$ 3 units in the second place of decimals. At least two determinations were made for each solution and the mean was taken.

The tip of the stalagmometer was freed from grease by being dipped in chromic acid solution before each determination and the whole apparatus was similarly cleansed at intervals. The drop number for water was checked from time to time and found to remain quite constant at 55·55 drops.

Materials.—As in the previous investigation, the hydrochloric acid employed was the pure commercial product and the cobalt chloride was Kahlbaum's purest, free from iron and nickel. All the water used was the laboratory distilled water, redistilled with precautions to preclude contamination by dust or grease.

Solutions.—Three stock solutions were prepared: cobalt chloride in water (120 g. of $CoCl_2,6H_2O$ per litre), cobalt chloride in concentrated hydrochloric acid (120 g. of $CoCl_2,6H_2O$ per litre), and hydrochloric acid in water. Their concentrations were adjusted to exactly the same values as those employed in the previous investigation. All the other solutions were prepared from these by dilution in the manner already described (*loc. cit.*).

Note on the Density of Aqueous Hydrochloric Acid.—It was not stated in the previous paper that in preparing the stock solution of hydrochloric acid by diluting the fuming acid, the solutions were cooled in iced water to minimise loss of acid. The stock solution was therefore 10·63*N* at 0° = 32·88% of HCl (by weight). In the present investigation, a solution of the acid having exactly the same density was found by titration against pure sodium carbonate to be 10·48*N* at 18°. The solution therefore contained 32·80% of HCl, a figure in good agreement with that previously found. The densities of the series of solutions prepared by diluting the stock solution were checked and found to agree with those obtained previously to within 1 unit in the fourth place of decimals.

In order to complete the series of values up to the fuming acid, the densities and viscosities of three more concentrated solutions have been determined; these are shown in Table I together with

the true normality of the solution at 18° and the composition by volume and by weight. The concentrations are correct to 0·2%, the densities to within 2 units in the fourth place of decimals and the viscosities to within 0·1%.

TABLE I.

Densities and Viscosities of Aqueous Solutions of Hydrochloric Acid.

Concentration of HCl.					
Normality, $N_{18°}$.	% by vol.	% by weight.	Relative density, $d^{20°}_{20°}$.	Absolute density, $d^{20°}_{4°}$.	Viscosity, $\eta_{20°}$.
0	0	0	1·0000	0·9982	0·01005
1·048	3·821	3·757	1·0186	1·0168	0·01065
2·096	7·642	7·385	1·0364	1·0346	0·01125
3·144	11·46	10·89	1·0536	1·0518	0·01187
4·192	15·28	14·29	1·0707	1·0689	0·01251
5·240	19·11	17·59	1·0871	1·0852	0·01323
6·288	22·93	20·80	1·1036	1·1016	0·01408
6·498	23·69	21·43	1·1067	1·1048	0·01430
6·812	24·84	22·37	1·1112	1·1092	0·01452
7·126	25·98	23·30	1·1162	1·1142	0·01482
7·336	26·75	23·91	1·1195	1·1176	0·01500
7·860	28·66	25·43	1·1275	1·1255	0·01555
8·384	30·57	26·94	1·1355	1·1335	0·01611
9·432	34·39	29·90	1·1507	1·1487	0·01731
10·48	38·21	32·80	1·1657	1·1637	0·01870
11·48	41·86	35·53	1·1789	1·1768	0·02004
12·83	46·78	39·14	1·1957	1·1935	0·02183
13·38	48·78	40·61	1·2020	1·1998	0·02266

The curve obtained on plotting the densities against the % of HCl by weight is almost a straight line up to 33%, being only very slightly concave to the axis of concentration. The last three values, however, fall below the extended curve, which is in agreement with the values recorded by other observers (Landolt and Bornstein's Tables, 1923, p. 394).

Results.

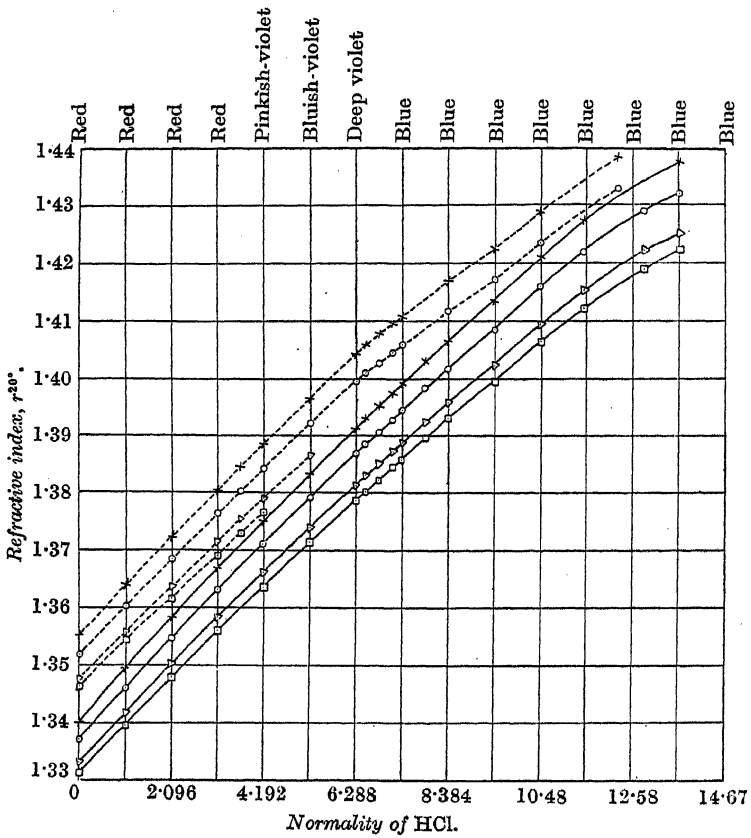
Refractive Indices.—The values of the refractive indices of the solutions of hydrochloric acid only, measured as already described, are given in Table II, and plotted against the normality of the solution in Fig. 1. It is seen that almost throughout their entire length all four curves exhibit a gradual increase of concavity to the axis of concentration. They fall more rapidly near the end, the values for the two highest concentrations of acid being lower than those anticipated from the general course of the curves. Each of the curves is expressed with very fair accuracy by an equation of the form

$$r_{\text{sol.}} = r_{\text{water}} + xN - yN^2,$$

where N is the normality of the solution and x and y are constants.

FIG. 1.

Colour of the cobalt solution in transmitted light.



Dotted line curves : Solutions of hydrochloric acid + cobalt chloride.
Full-line curves : Solutions of hydrochloric acid only.

Refractive index for the G′ *line shown thus :* ×.
" " " F " " " ⊙.
" " " D " " " △.
" " " C " " " ⊡.

The values calculated from the equations

$$r_C^{20°} = 1{\cdot}33117 + 0{\cdot}008090N_{18°} - 0{\cdot}0000862N_{18°}^2$$
$$r_D^{20°} = 1{\cdot}33299 + 0{\cdot}008330N_{18°} - 0{\cdot}0001000N_{18°}^2$$
$$r_F^{20°} = 1{\cdot}33703 + 0{\cdot}008630N_{18°} - 0{\cdot}0001083N_{18°}^2$$
$$r_{G'}^{20°} = 1{\cdot}34017 + 0{\cdot}008850N_{18°} - 0{\cdot}0001129N_{18°}^2$$

are given in italics in the columns next to the observed values in

TABLE II.

Refractive Indices of Aqueous Solutions of Hydrochloric Acid.

Conc. of HCl,		$r_C^{20°}$.		$r_D^{20°}$.		$r_F^{20°}$.		$r_{G'}^{20°}$.	
$N_{18°}$.	%.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0	0	1·33117	*1·33117*	1·33299	*1·33299*	1·33703	*1·33703*	1·34017	*1·34017*
1·048	3·757	1·33938	*1·33956*	1·34173	*1·34161*	1·34599	*1·34595*	1·34944	*1·34933*
2·096	7·385	1·34786	*1·34775*	1·35007	*1·35001*	1·35464	*1·35464*	1·35824	*1·35823*
3·144	10·89	1·35594	*1·35575*	1·35815	*1·35819*	1·36305	*1·36309*	1·36684	*1·36687*
4·192	14·29	1·36357	*1·36357*	1·36603	*1·36615*	1·37111	*1·37130*	1·37521	*1·37529*
5·240	17·59	1·37135	*1·37120*	1·37387	*1·37389*	1·37922	*1·37927*	1·38339	*1·38344*
6·288	20·79	1·37863	*1·37863*	1·38127	*1·38142*	1·38686	*1·38701*	1·39121	*1·39136*
6·408	21·43	1·38027	*1·38010*	1·38304	*1·38291*	1·38850	*1·38853*	1·39302	*1·39291*
6·812	22·37	1·38230	*1·38223*	1·38503	*1·38509*	1·39059	*1·39079*	1·39517	*1·39522*
7·126	23·30	1·38442	*1·38444*	1·38713	*1·38727*	1·39281	*1·39303*	1·39745	*1·39751*
7·336	23·91	1·38592	*1·38589*	1·38867	*1·38872*	1·39449	*1·39451*	1·39903	*1·39901*
7·860	25·43	1·38962	*1·38945*	1·39238	*1·39229*	1·39830	*1·39817*	1·40305	*1·40276*
8·384	26·94	1·39294	*1·39295*	1·39572	*1·39580*	1·40169	*1·40176*	1·40646	*1·40643*
9·432	29·90	1·39945	*1·39981*	1·40218	*1·40266*	1·40851	*1·40879*	1·41350	*1·41360*
10·48	32·80	1·40654	*1·40649*	1·40950	*1·40931*	1·41600	*1·41557*	1·42111	*1·42052*
11·48	35·53	1·41224	*1·41269*	1·41542	*1·41544*	1·42209	*1·42183*	1·42743	*1·42688*
12·83	39·14	1·41907	—	1·42232	—	1·42915	—	1·43454	—
13·38	40·61	1·42203	—	1·42522	—	1·43222	—	1·43784	—

Table II. It is seen that the agreement is quite good up to a concentration of $10N$.

The refractive indices of the solutions containing cobalt are given in Table III and plotted against the normality of the acid in Fig. 1 with those for the solutions of acid only. It is seen that the curves are not smooth. There is an obvious break in the continuity, and each curve ultimately tends to become parallel with the corresponding curve for the solutions of acid only.

TABLE III.

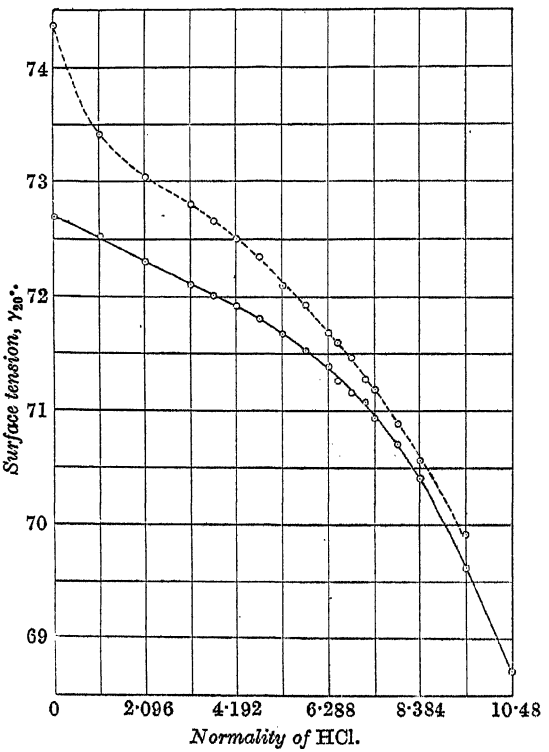
Refractive Indices of $CoCl_2 + HCl$ *Solutions and Differences from Corresponding* HCl *Solutions.*

Normality of acid, $N_{18°}$.	$r_C^{20°}$.	Difference $\times 10^5$.	$r_D^{20°}$.	Difference $\times 10^5$.	$r_F^{20°}$.	Difference $\times 10^5$.	$r_{G'}^{20°}$.	Difference $\times 10^5$.
0	1·34621	1504	1·34744	1445	1·35172	1469	1·35524	1507
1·048	1·35437	1499	1·35564	1391	1·36019	1420	1·36390	1446
2·096	1·36147	1361	1·36367	1360	1·36844	1380	1·37236	1412
3·144	1·36899	1305	1·37142	1327	1·37646	1341	1·38056	1372
3·668	1·37283	1308	1·37541	1332	1·38039	1331	1·38463	1361
4·192	1·37655	1298	1·37906	1303	1·38435	1324	1·38864	1343
4·716			1·38294	1299	1·38828	1312	1·39270	1340
5·240			1·38670	1283	1·39225	1303	1·39673	1334
6·288					1·39957	1271	1·40415	1294
6·498					1·40093	1243	1·40568	1266
6·812					1·40269	1210	1·40767	1250
7·126					1·40449	1168	1·40932	1187
7·336					1·40583	1134	1·41065	1162
8·384					1·41169	1000	1·41693	1047
9·432					1·41726	875	1·42268	918
10·48					1·42366	766	1·42913	802
12·26					1·43301	641	1·43853	673

If the cobalt atom were similarly associated in all these solutions, the refractive index should change regularly with increasing con-

centration of acid, as it does with the solutions of acid alone. Since this is not so, it follows that the cobalt atom undergoes a change in its association as the concentration of acid is increased; a suggestion as to the nature of this change has been given on p. 2039 and its course may be followed by considering the differences of the refractive indices of corresponding solutions. The values

FIG. 2.



Upper curve: Solutions of hydrochloric acid + cobalt chloride.
Lower curve: Solutions of hydrochloric acid only.

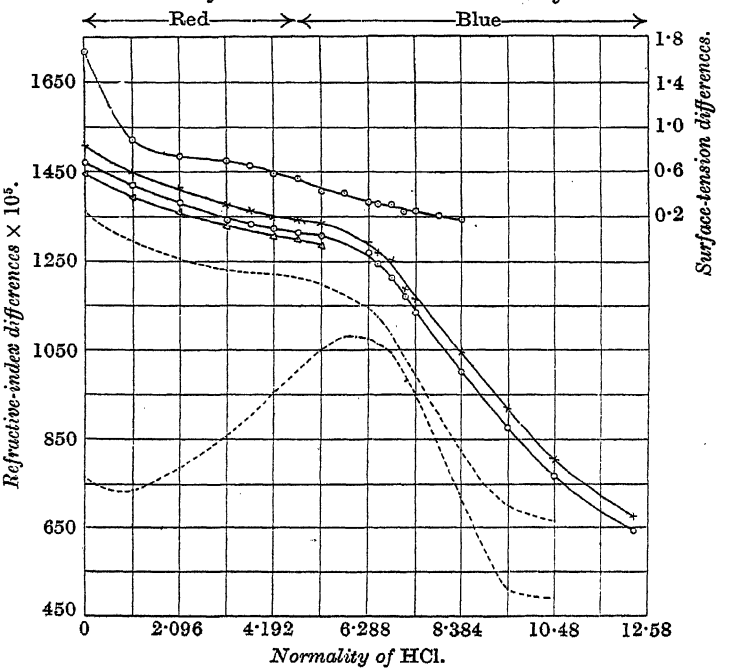
obtained on subtracting the refractive indices of the solutions of hydrochloric acid alone from those of the corresponding solutions containing cobalt are given in Table III and plotted against the normality of the acid in Fig. 3.

The resulting curves are precisely similar to the curve obtained in the previous investigation by plotting the density differences against the concentration of acid. They exhibit well-marked inflexions at the same concentration of acid as the inflexion of the

density-differences curve and as the maximum of the viscosity-differences curve (both of which are reproduced in Fig. 3 for comparison). It is seen that towards the end of its course each curve is flattening out (although not as sharply as the density-differences curve) to become parallel to the axis of concentration, thus indicat-

FIG. 3.

Colour of the cobalt solution in transmitted light.



Upper full-line curve : Surface-tension differences.
Lower full-line curves : Refractive-index differences.

For the G′ line, shown thus : ×.
" " F " " " ⊙.
" " D " " " △.

Upper dotted-line curve : Density differences.
Lower dotted-line curve : Viscosity differences.

ing that the change to the $CoCl_4''$ configuration is nearing completion, where further increase in the concentration of acid could no longer affect the state of the cobalt atom.

The refractive index of the blue form is evidently less than that of the red. As the concentration of acid is increased and the change from red to blue proceeds, the curve falls continuously but not regularly. The diminution of the difference of refractive index,

like that of the density difference, takes place at first very gradually and then very rapidly. The suggestion offered to account for this feature in the density-differences curve also explains the same form of the refractive index-differences curve. The $Co(H_2O)_6^{\cdot\cdot}$ ions are progressively converted into $CoCl_4''$ ions, and as these are oppositely charged there is a powerful attraction between them. Evidently this attraction will be a maximum when equal numbers are present in the solution, and it is suggested that this condition obtains at the point of inflexion.

Surface Tensions.—The values of the surface tensions for the two series of solutions are given in Table IV and plotted in Fig. 2. Previous determinations of the surface tension of some aqueous solutions of hydrochloric acid alone have been made by Volkmann (see Landolt and Bornstein's Tables, 1923, p. 238) using the capillary-rise method. The values are in fair agreement with those now reported, which lie on a smooth curve. An equation has not been found to express the whole curve, but if the logarithm of the

TABLE IV.

Surface Tensions.

1.	2.	3.	4.	5.	6.
		Surface tension of			
Conc. of HCl,		$CoCl_2$+HCl.	HCl alone.		Difference,
$N_{18°}$.	%.	$\gamma_{20°}$.	$\gamma_{20°}$ (obs.).	$\gamma_{20°}$ (calc.).	(3—5).
0	0	74·36	72·69	—	1·67
1·048	3·757	73·41	72·52	—	0·89
2·096	7·385	73·04	72·30	—	0·74
3·144	10·89	72·80	72·10	*72·10*	0·70
3·668	12·63	72·66	72·00*	*72·01*	0·65
4·192	14·29	72·50	71·91	*71·92*	0·58
4·716	15·97	72·34	71·80*	*71·80*	0·54
5·240	17·59	72·09	71·67	*71·67*	0·42
5·764	19·20	71·92	71·52	*71·52*	0·40
6·288	20·79	71·68	71·38	*71·36*	0·32
6·498	21·43	71·59	71·26	*71·28*	0·31
6·812	22·37	71·46	71·15	*71·16*	0·30
7·126	23·30	71·27	71·07	*71·03*	0·24
7·336	23·91	71·18	70·92	*70·94*	0·24
7·860	25·43	70·88	70·70	*70·68*	0·20
8·384	26·94	70·56	70·40	*70·39*	0·17
9·432	29·90	69·91	69·62	*69·66*	0·25
10·48	32·80	—	68·71	*68·71*	—

(Column 2 refers only to the solutions of hydrochloric acid alone.)

* These two values are read from the curve shown in Fig. 2.

difference, Δ, between the surface tension of water and that of each solution be plotted against the concentration of the solution, all the points except the first three lie on a perfectly straight line. The equation to the line is

$$\log \Delta = 0{\cdot}1130N_{18°} - 0{\cdot}5850$$

where $\Delta = \gamma_{water} - \gamma_{sol.}$, and N_{18} is the normality of the solution at 18°. The values of the surface tension calculated from this expression are given in column 5 of Table IV. Comparing them with the observed values in column 4, it is seen that the agreement is within the limits of experimental error.

It was found impossible to get very concordant values of the drop number with the more concentrated acid solutions. They indicate, however, that the surface tensions of these solutions are progressively higher than those anticipated from the general course of the curve. It will be recalled that the densities of these solutions were lower than demanded by the form of the density curve.

The curve for the solutions containing cobalt, on the other hand, obviously consists of two parts, the first (for lower concentrations of acid) being convex to the axis of concentration, and the second (for higher concentrations of acid) being concave to this axis, and eventually becoming parallel to the curve for the solutions of acid alone.

The change in the association of the cobalt atom may again be followed by examining the differences of the surface tensions of the solutions containing cobalt and the corresponding solutions containing acid only. These differences are given in column 6 of Table IV and are plotted against the normality of acid in Fig. 3. It is seen that the curve is again of the same type as the density-differences curve and the refractive index-differences curves, but it differs from these in two important particulars.

The first of these is that the curve falls away rapidly from the initial value, whereas both the density-differences and the refractive index-differences curves fall off gently from the beginning. This characteristic of the surface tension-differences curve is readily explained. It is seen from the values of the surface tensions in Table IV and from the curves in Fig. 2 that the first solution in the series containing cobalt (*i.e.*, aqueous cobalt chloride alone) has a surface tension greater than that of water; so also have the solutions immediately following. That is, the cobalt atom in its red association, $Co(H_2O)_6^{\cdot\cdot}$, *raises* the surface tension of water. It follows from the Gibbs equation that the concentration of this ion in the surface layer is *less* than that in the bulk of the solution.

It is evident from the curves in Fig. 2 that the blue solutions (those having a high concentration of acid) have a surface tension only slightly higher than the corresponding solutions containing acid alone. Assuming that the whole of the acid is " free " in these cobalt solutions, as in the solutions of acid alone, it follows that the cobalt atom in its blue association, $CoCl_4''$, also raises the surface tension of water, but to a far smaller extent than does the

red $Co(H_2O)_6^{\cdot\cdot}$. It is quite probable, however, since the acid is not wholly free but partly bound in the form of these complex ions, that the surface tension of the blue solutions is actually less than that of solutions of acid alone having a concentration equal to that of the "free" acid. In this event, the blue form, $CoCl_4''$, *lowers* the surface tension of water, and in accordance with the Gibbs equation its concentration in the surface layer is *greater* than in the bulk.

Even if the blue form raises the surface tension, it follows that for a given bulk concentration of cobalt, its concentration in the surface layer would be greater than that of the red form. When, therefore, the first introduction of acid to the cobalt solution results in the conversion of some $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions, the same change takes place in the surface layer to a far greater degree. The increase in concentration of the blue form is therefore far greater in the surface layer than in the bulk of the solution. The surface tension, which is a purely surface phenomenon, is a measure of this change, so that the surface tension-differences curve falls rapidly with the initial increases in acid concentration, whereas the density-differences curve and the refractive index-differences curves, indicating the effect in the bulk of the solution, fall away gradually.

The second particular in which the surface tension-differences curve differs from the others is that it exhibits its inflexion at a different concentration of acid. This also is to be expected and is explicable on the same reasoning. It has been suggested that the point of inflexion in the density-differences curve and in the refractive index-differences curves and also the maximum in the viscosity-differences curve occur when the solution contains equal amounts of the two kinds of ions, $Co(H_2O)_6^{\cdot\cdot}$ and $CoCl_4''$, since the attraction between them will then be greatest. It is now suggested that the point of inflexion in the surface tension-differences curve corresponds to the concentration of acid at which the same conditions obtain in the surface layer. Since the blue form accumulates in the surface layer to the exclusion of the red form, it follows that there will be equal amounts of each in the surface layer before this state is reached in the bulk of the solution. The surface tension-differences curve should therefore exhibit inflexion before the corresponding curves for the other properties which are dependent on the conditions in the bulk. It is seen from Fig. 3 that this is so.

It should be noted that although replacement of half the red form by the blue occurs in the surface layer sooner than in the bulk, the complete replacement cannot occur until this change is also

complete in the bulk. So long as any of the red form remains in the solution, a corresponding amount will be present in the surface layer, and it is not until all the red form has been converted in the solution that the same state is reached in the surface layer. The surface tension-differences curve should therefore not flatten out and become parallel to the axis of concentration sooner than the other curves, but at the same concentration of acid. It is seen from Fig. 3 that the curve falls continuously from the point of inflexion and has not become parallel over the range examined, but there are indications that this condition will be reached as with the other curves.

The Colour Change.—In the previous investigation, the colours of the cobalt solutions recorded were those observed by viewing thin layers against a white ground. In the present paper the colours of layers 5 cm. thick viewed in transmitted daylight are given at the head of Fig. 1.

The solutions having an acid concentration up to 3·144*N* are definitely red when examined in either thin or thick layers. Those having a concentration greater than 6·288*N* are green in very thin layers, but definitely blue with no trace of green in thicker layers. This dichroism is very marked.

Whereas these definitely red and blue solutions are clear and "clean," those lying within the limits stated are dull and "muddy" in appearance. In thin layers, the colour is indefinite. Thus the 4·192*N*-solution was previously described as brownish-red; in a thick layer, however, it is pinkish-violet, being definitely reddish with a tinge of blue. The 5·240*N*-solution, which is the most indefinite, was called a dull brown, but would have been better described as a dull amethyst, for even in thin layers it has a distinct blue tinge. In thicker layers the solution is definitely blue with a faint tinge of red. The 6·288*N*-solution is a very deep violet. The change in colour is therefore gradual and extends over a fair range of acid concentration. The 4·192*N*-solution being more red than blue, and the 5·240*N*-solution being more blue than red, the maximum colour change occurs between these concentrations of acid, as indicated at the head of Fig. 3. The 4·716*N*-solution, mid-way in acid concentration between these two, appears to be very nearly half red and half blue.

It was pointed out in the previous investigation that the point of inflexion in the density-differences curve and the maximum in the viscosity-differences curve do not coincide with the maximum change in colour, but at a considerably higher concentration of acid. The same is now seen to be true for the refractive index-differences curve. The colour change therefore takes place before

even half the cobalt has been transformed from the red to the blue association and this is in accordance with the fact already pointed out, that the blue form is far more intense than the red.

It should be noted that the concentration of acid at which the two forms are in equal amount in the surface layer, as indicated by the surface tension-differences curve, also does not correspond to the concentration at which the change of colour occurs.

Summary.

1. The refractive indices and surface tensions of a series of aqueous solutions containing a constant amount of cobalt chloride and increasing amounts of hydrochloric acid have been determined.

2. The same constants of an exactly similar series containing hydrochloric acid alone have also been measured.

3. The differences in the values for corresponding solutions bring to light the effect of the acid on the cobalt in solution.

4. The curve showing the differences in refractive index plotted against the concentration of acid is exactly similar to that of the density differences found in a previous investigation. The point of inflexion in both occurs at the same concentration of acid and is accounted for on the same reasoning.

5. The curve showing the differences in surface tension is also similar, but has a sharp initial fall and exhibits its point of inflexion at a lower concentration of acid. These two differences are wholly explained by the facts (*a*) that the surface tension is a measure of the conditions prevailing in the surface layer while the other properties are a measure of those in the bulk of the solution, and (*b*) that the relative concentrations of the red and the blue cobalt ions in the surface layer are different from those in the bulk under any given conditions.

6. The change in colour of the cobalt solutions with increasing acid concentration is discussed.

The author would express his sincere thanks to Prof. F. L. Pyman, F.R.S., for giving him every facility for prosecuting this work.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, June 4th*, 1927.]

CCLXIX.—*Formation and Decomposition of Ketone Cyanohydrins, with Special Reference to some Compounds recently classified as such.*

By ARTHUR LAPWORTH, RICHARD HELMUTH FRED MANSKE, and EDWIN BREW ROBINSON.

IN a recent paper (*Ber.*, 1927, **60**, 586) Houben and Pfankuch described some new nitriles two of which were considered to be the stereoisomeric cyanohydrins of camphor. These workers commented on the remarkable stability of these nitriles, which did not show any tendency to dissociate into hydrogen cyanide and ketone; but having also found that the direct union of hydrogen cyanide and camphor cannot be effected, they concluded that these observations illustrate the rule that "ein Korper, der schwer entsteht, meistens schwer wieder zerfällt" (*loc. cit.*, p. 587).

Houben and Pfankuch described another new nitrile which they regarded as "menthon-cyanohydrin" (*loc. cit.*, p. 599). They did not state specifically that this compound has the same remarkable stability as the supposed camphor cyanohydrins, but, as they were able to purify it (apparently without adopting any special precautions) from boiling ligroin and to hydrolyse it with methyl-alcoholic potassium hydroxide, there can be no doubt that the compound was much more stable than most of the known cyanohydrins of other simple ketones.

Passerini, in a still more recent paper (*Ber.*, 1927, **60**, 1201, 1202), accepts the views of Houben and Pfankuch, but finds that the supposed "menthon-cyanohydrin" described by these authors is converted on hydrolysis with acids into a lactone, and infers that here "das Hydroxyl des Menthon-cyanohydrin in den Menthan-Ring wandert." Such a migration in a saturated compound has no parallel within the knowledge of the present authors.

A long series of measurements of equilibria in systems containing cyanohydrin, hydrogen cyanide and ketone (or aldehyde) in aqueous alcohol has been made in these laboratories during the last 3 years and among the cases studied were those comprising camphor and menthone respectively. It was found that, out of some 60 ketones and aromatic aldehydes examined, only 2, benzophenone and camphor, gave no detectable amounts of cyanohydrin by direct combination with hydrogen cyanide. With the others, a sensibly constant equilibrium condition was attained within 24 to 36 hours at most in aqueous alcohol, if a very small proportion of tripropylamine was present as catalyst. The dissociation constants of the cyanohydrins varied very widely, ratios of extremes observed being

at least 1 : 25,000, and the failure of camphor and benzophenone to yield measurable quantities of cyanohydrin is doubtless to be ascribed to the exceptionally high dissociation constants of the cyanohydrins rather than to catastrophic disappearance of reaction velocity.

It is quite otherwise in the case of menthone, the cyanohydrin * of which is formed quite readily in the cold, the time required in the above conditions to attain a concentration practically identical with the equilibrium value not exceeding 24 hours.

Experiment A illustrates some of these statements: Menthone (11·38 g.), 2 c.c. of ethyl alcohol containing 0·24 g. of tripropylamine, and 5 c.c. of anhydrous hydrogen cyanide dissolved in cold dry methyl alcohol (about 30 c.c.) were mixed and left over-night in a stoppered flask, previous experience having shown that further contraction (initially attendant on combination) is inappreciable after such a period. The vessel was then opened, the contents made up to 50 c.c. with more dried methyl alcohol, and the flask again closed with a waxed stopper and allowed to remain in an ice-chest for 60 hours, a period considerably exceeding that (24—36 hours) which previous experiments, under not wholly dissimilar conditions, had shown to be amply sufficient for the attainment of a practically steady state.† The solution was then analysed by a method based on that of Ultée (*Rec. trav. chim.*, 1909, **28**, 248), which depends on the fact that in presence of mineral acid, silver nitrate in the cold precipitates only cyanidion which is not in combination with the aldehyde or ketone. An aliquot portion of the solution was removed and at once added to excess of standard silver nitrate solution acidified with nitric acid, the whole being shaken, and the silver cyanide removed by filtration. The excess of silver in the filtrate was determined by titration with standard thiocyanate in the usual way. The free hydrogen cyanide present in the original 50 c.c. of solution was thus found to be 1·95 g.

Another portion of the solution was removed and allowed to remain in the cold with five times its bulk of *N*-sodium hydroxide for 45 minutes. The whole was acidified with nitric acid and mixed with excess of standard silver nitrate and the excess of silver was determined as before. The total hydrogen cyanide found in this way was 3·49 g. (comparing favourably with 3·53 g. found in the

* Strictly speaking, as menthone itself is a mixture of two dynamic isomerides, each of which can theoretically give rise to two stereoisomeric addition compounds with hydrogen cyanide, the cyanohydrin formed as above must be a mixture of four isomerides.

† A blank experiment in which the menthone was omitted showed that the total amount of hydrogen cyanide remaining after these manipulations would be approximately 3·53 g. if no combination had taken place.

blank experiment above mentioned). It is probable that a minute but hardly measurable quantity of the sodium derivative of the cyanohydrin remains in equilibrium with menthone and cyanidion in presence of sodium hydroxide:

$$C_{10}H_{18}O + CN' \rightleftharpoons C_{10}H_{18}(CN)\cdot O'.$$

From the titres, it may be deduced (1) that at equilibrium under the conditions specified above, 1 mol. of menthone is converted to the extent of about 0·8 mol. into cyanohydrin, in equilibrium with which 0·2 mol. of unchanged menthone remains with about 1 mol. of uncombined hydrogen cyanide, (2) that menthone cyanohydrin is almost completely converted into menthone and sodium cyanide by cold *N*-sodium hydroxide in not more than 45 minutes, the rapid acidification preventing appreciable recombination.

While the equilibrium may be effectively "frozen" by excess of mineral acid in aqueous or dilute alcoholic solution (as is shown by the failure of silver nitrate to decompose the cyanohydrin in these circumstances), it has not been found possible to separate the cyanohydrin from unchanged menthone owing to the instability of the former. It is quite easy to convert menthone to the extent of 90% into mixed cyanohydrins with excess of anhydrous hydrogen cyanide in presence of a trace of tripropylamine; but when attempts were made to remove hydrogen cyanide at the ordinary temperature by the use of a vacuum, even after adding some excess of hydrogen chloride in ether in the endeavour to stabilise the cyanohydrin, the latter underwent considerable decomposition and in the end constituted only about 30% of the residual oil.

On subjecting the equilibrium mixtures to hydrolytic action of mineral acids, including sulphuric acid, concentrated or dilute, in the cold, no evidence was obtained of the formation of any acid amide or carboxylic acid, and Pinner's method for the conversion of nitriles into imino-ethers in ethereal solution also gave negative results; the nitrile group is, in fact, extremely resistant to cold acid hydrolysts. If the temperature be raised, thermal dissociation occurs and hydrogen cyanide is lost, again before any effective hydrolysis has taken place. With alkalis, as has been demonstrated, the cyanohydrin is almost quantitatively decomposed even in the cold in a short time—probably within a few seconds. The great speed at which equilibrium is reached from either side in systems comprising ketone and cyanohydrin in presence of considerable concentrations of hydroxylion or cyanidion or both is perhaps not generally realised. *Experiment B* is described to illustrate the last point.

B. Cold saturated aqueous potassium cyanide (1 c.c.) at about

20° is shaken in a test-tube with 0·2 c.c. of *cyclo*hexanone which has been purified through the bisulphite compound. The ketone, at first immiscible, very quickly disappears, if the temperature is initially about 15°, a clear solution being formed with rise of temperature; then, as a rule, crystals of the potassium derivative of the cyanohydrin almost at once begin to appear and the whole sets, within about 30 seconds from the beginning of the experiment, to a semi-solid mass.

How little the concentration of *free* hydrogen cyanide affects the addition process may also be observed by repeating the experiment with the previous addition of 0·5 c.c. of 30% aqueous potassium hydroxide to the potassium cyanide. Although the concentration of free hydrogen cyanide due to salt hydrolysis must be reduced thereby many thousand-fold, the same phenomena are observed, while the time taken for setting is not more than doubled. The apparent decrease in speed is doubtless due in the main to the salting-out action of the potassium hydroxide reducing the already small solubility of the *cyclo*hexanone in the aqueous phase.

Observations already mentioned show that menthone cyanohydrin is readily formed and decomposed even in the cold in alkaline media and therefore, if the phenomena just described are not reproduced when menthone is used instead of *cyclo*hexanone, it is not because reaction is indefinitely delayed, but because the dissociation constants of menthone cyanohydrin and of its potassium derivative are much higher than those of *cyclo*hexanone cyanohydrin and of its potassium derivative respectively.* If, therefore, the compound described by Houben and Pfankuch were, in fact, menthone cyanohydrin, then at a very early stage in the alkaline hydrolysis which they carried out (*loc. cit.*, p. 600) equilibrium must have been attained, and this equilibrium should be reached no less rapidly by simply boiling menthone with potassium cyanide and potassium hydroxide in methyl-alcoholic solution, and with similar results on allowing hydrolysis to proceed. *Experiment C* was therefore carried out.

C. Menthone (10 g.) with potassium cyanide (10 g., or 2·5 mols.) and methyl alcohol (100 c.c.) was heated on the steam-bath for 48 hours. (A small portion of the product was removed at this point and worked up for carboxylic acid, but none could be detected.) Potassium hydroxide (25 g.) was next added and the heating was continued for a further 70 hours. On working up the whole for carboxylic acid, 1·9 g. of oily product, sparingly soluble in water but

* The dissociation constants of the two cyanohydrins in aqueous alcoholic solution at the ordinary temperature have been measured by one of us (R. H. F. M.) and found to be roughly in the ratio 72 : 1.

readily soluble in aqueous sodium carbonate, were isolated. Doubtless Houben and Pfankuch would have commented on such a poor yield after so prolonged a period of heating, but they do not mention either. It may be added that on attempting to convert the acid material into amide by the method used by Houben and Pfankuch only a small proportion of the product was soluble in hot ligroin, and even that portion failed to yield any crystalline solid.

Conclusions.—True menthone cyanohydrin, *i.e.*, the mixture of cyanohydrins produced by addition of hydrogen cyanide to ordinary menthone, is readily formed and decomposed reversibly in solutions which are at all alkaline and its properties indicate that Houben and Pfankuch were dealing with quite another compound. The characters ascribed by these workers to the compounds which they describe as camphor cyanohydrins are also at variance with those of all known ketone cyanohydrins.

It is suggested that a transformation of the Wagner type occurs when the nitrogen atom is separated from carbon in the experiments described by Houben and Pfankuch.

THE UNIVERSITY, MANCHESTER. [*Received, July 5th*, 1927.]

CCLXX.—l-*Methylephedrine, an Alkaloid from* Ephedra *Species.*

By SYDNEY SMITH.

THE Chinese drug Ma Huang derived from an *Ephedra* species has become of importance in Western medicine as the source of *l*-ephedrine, an alkaloid which has recently been found to possess a physiological action resembling that of adrenaline. In addition to *l*-ephedrine the drug contains *d*-ψ-ephedrine, and another alkaloid, the subject of the present communication, has now been isolated.

The constitutions of *l*-ephedrine and *d*-ψ-ephedrine

(OH·CHPh·CHMe·NHMe)

have been established beyond doubt by syntheses of the racemic bases and their resolution into the corresponding enantiomorphic forms, two of which are identical with the naturally occurring alkaloids *l*-ephedrine and *d*-ψ-ephedrine. The empirical formula and properties of the new alkaloid suggested that it was probably the *N*-methyl derivative of either *l*-ephedrine or *d*-ψ-ephedrine. The *N*-methyl derivatives were therefore prepared by methylation of the natural bases and it was found that the m. p. and specific rotation of *l*-methylephedrine were identical with those of the new alkaloid. Comparison of the m. p. and specific rotation of the

corresponding hydrochlorides and the methiodides afforded ample confirmation that the new alkaloid is identical with *l*-methylephedrine, $OH{\cdot}CHPh{\cdot}CHMe{\cdot}NMe_2$.

EXPERIMENTAL.

The syrupy alkaloidal residue obtained in the manufacture of ephedrine, freed as completely as possible from *l*-ephedrine and *d*-ψ-ephedrine, was purified by distillation under reduced pressure and neutralised with aqueous oxalic acid and the solution was evaporated to dryness. The residue on extraction with alcohol gave an alcohol-soluble fraction, which was dissolved in water and treated with a saturated aqueous solution of picric acid. The oil which first separated became solid on standing, and subsequent crops separated in a crystalline condition. The picrate was treated with hydrochloric acid and ether, and the resulting solution of the hydrochloride evaporated to dryness. The residue, after several crystallisations from alcohol, gave *l-methylephedrine hydrochloride* in stout, colourless tablets, m. p. 188—189° (corr.) (Found: C, 61·3; H, 8·3; Cl, 16·2. $C_{11}H_{17}ON,HCl$ requires C, 61·2; H, 8·4; Cl, 16·4%). It is readily soluble in water, less soluble in alcohol, and sparingly soluble in acetone. In water solution, it had $[\alpha]_D$ −29·8° ($c = 4{\cdot}6$).

l-Methylephedrine, prepared by addition of concentrated potassium hydroxide solution to a solution of *l*-methylephedrine hydrochloride in water, separated as an oil which rapidly solidified. It crystallised readily from methyl alcohol in stout needles, m. p. 87—88° (corr.). Previously recorded values are 59—62° (Miller, *Arch. Pharm.*, 1902, **240**, 481), 78° (Eberhard, *ibid.*, 1915, **253**, 65), 84° (Nagai, Abstract by Chen and Kao, *J. Amer. Pharm. Assoc.*, 1926, **15**, 632) (Found: C, 73·5; H, 9·4. Calc. for $C_{11}H_{17}ON$: C, 73·7; H, 9·6%). The base can be titrated with standard acid with methyl-red as indicator: 0·7956 g. required 44·4 c.c. of 0·1*N*-sulphuric acid. $C_{11}H_{17}ON$ requires 44·4 c.c. In methyl alcohol it had $[\alpha]_D$ −29·2° ($c = 3{\cdot}0$). When treated with methyl iodide in methyl-alcoholic solution, it gave a *methiodide* which crystallised from alcohol in stout tablets, m. p. 212—213° (corr.) and had $[\alpha]_D$ −21·8° ($c = 2{\cdot}9$) (Found: I, 39·6. $C_{12}H_{20}ONI$ requires I, 39·5%).

Methylation of l-*Ephedrine.*—*l*-Ephedrine (28·4 g.), dissolved in methyl alcohol (28·4 c.c.), was boiled on a water-bath, and methyl iodide (27 g.) in methyl alcohol (27 c.c.) was added slowly. The solution was boiled for 2 hours, concentrated under diminished pressure, and treated with potassium hydroxide solution and ether; 23·6 g. of the methiodide then separated. The alkaline liquor was

extracted with ether and added to the first ethereal extract. After drying over potassium carbonate, the ethereal solution was distilled, the residual base neutralised with aqueous oxalic acid, and successive crops of *l*-ephedrine oxalate, m. p. 249° (corr.), were removed. The final syrupy mother-liquor was treated with excess of potassium hydroxide solution; an oil then separated which rapidly solidified. It melted at 86—87° (corr.) after crystallisation from light petroleum and at 87—88° (corr.) after a further crystallisation from methyl alcohol. When mixed with the alkaloid obtained from Ma Huang, it showed no depression in m. p. (Found: C, 73·7; H, 9·4. Calc. for $C_{11}H_{17}ON$: C, 73·7; H, 9·6%). It had $[\alpha]_D$ −29·5° in methyl alcohol ($c = 4·5$).

The base was dissolved in ether and neutralised with hydrogen chloride. On crystallisation from alcohol the hydrochloride formed colourless tablets, m. p. 188—189° (Found: C, 61·4; H, 8·3; Cl, 16·4. Calc. for $C_{11}H_{17}ON,HCl$: C, 61·2; H, 8·4; Cl, 16·4%). It had $[\alpha]_D$ −29·8° in water ($c = 5·7$). There was no depression of the melting point after admixture with the hydrochloride obtained from Ma Huang.

l-Methylephedrine methiodide crystallises from alcohol in stout tablets, m. p. 212—213° (corr.) (Eberhard, *loc. cit.*, gave m. p. 204°). In aqueous solution it had $[\alpha]_D$ −21·3° ($c = 5·5$) (Found: I, 39·3. Calc. for $C_{12}H_{20}ONI$: I, 39·5%).

l-*Methylephedrine picrate* was prepared by adding a solution of the hydrochloride to a saturated aqueous solution of picric acid. It crystallised readily from alcohol and melted at 144° (corr.) (Found: C, 50·3; H, 4·5. $C_{17}H_{20}O_8N_4$ requires C, 50·0; H, 4·9%).

Methylation of d-*ψ*-*Ephedrine.*—*d*-*ψ*-Ephedrine (56·8 g.), dissolved in methyl alcohol (56·8 c.c.), was boiled on a water-bath, and methyl iodide (56·8 g.) added slowly. The mixture was boiled for 4 hours and treated with potassium hydroxide solution and ether; it then deposited crystals of the methiodide (24·1 g.). The alkaline liquor was extracted with ether and the united ethereal extracts were dried over potassium carbonate. After removal of the ether a crystalline residue (47·6 g.) was obtained which was fractionally crystallised from light petroleum; it then gave as a first crop 6·7 g. of crude *d*-*ψ*-ephedrine, m. p. 113°. Subsequent crops of low-melting base were obtained which were found by titration to consist of nearly pure methylephedrine.

The base was converted into the hydrogen tartrate and purified by recrystallisation from water.

d-*ψ*-*Methylephedrine hydrogen tartrate* crystallises in needles which melt at 84° (corr.) and, after drying in a vacuum over sulphuric acid, at 152° (corr.) (Found in air-dried salt: loss in a vacuum over

H_2SO_4, 10·0. $C_{11}H_{17}ON,C_4H_6O_6,2H_2O$ requires loss, 9·9%. Found in dried salt: C, 54·6; H, 6·9. $C_{11}H_{17}ON,C_4H_6O_6$ requires C, 54·7; H, 7·0%).

d-*ψ*-*Methylephedrine* was prepared by the addition of sodium hydroxide solution to a solution of the hydrogen tartrate in water. The base was extracted with ether and dried over potassium carbonate, and the ether removed by distillation. The residue crystallised readily on cooling and melted at 29—30° (corr.). Emde (*Arch. Pharm.*, 1906, **244**, 246) obtained the base as a thick oily liquid. It was recrystallised from light petroleum at −10°; thereafter it melted at 30° (corr.). d-*ψ*-*Methylephedrine* is readily soluble in the common organic solvents, and somewhat sparingly soluble in water (Found: C, 73·7; H, 9·4. $C_{11}H_{17}ON$ requires C, 73·7; H, 9·6%). In methyl alcohol it had $[\alpha]_D$ +48·1° ($c = 4·7$). It can be titrated with standard acid and methyl-red: 0·6689 g. required for neutralisation 37·2 c.c. of 0·1*N*-sulphuric acid. $C_{11}H_{17}ON$ requires 37·3 c.c.

d-*ψ*-Methylephedrine methiodide crystallises readily from alcohol; m. p. 216—217° (corr.) (Emde, *loc. cit.*, gave m. p. 205°) (Found: I, 39·4. Calc. for $C_{12}H_{20}ONI$: I, 39·5%). In aqueous solution it had $[\alpha]_D$ +34·7° ($c = 2·9$).

d-*ψ*-*Methylephedrine picrate* was prepared by addition of a solution of the hydrochloride to a saturated solution of picric acid in water. It crystallised readily from alcohol and melted at 152—153° (corr.) (Found: C, 50·4; H, 4·9. $C_{17}H_{20}O_8N_4$ requires C, 50·0; H, 4·9%).

The author's thanks are due to Mr. W. Ramsay for assistance in this investigation.

WELLCOME CHEMICAL WORKS,
DARTFORD.

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CCLXXI.—*The Use of Titanous Chloride in the Volumetric Estimation of Copper and Iron.*

By WILLIAM GIDLEY EMMETT.

IN the course of a research involving many analyses of cupric chloride solutions, copper was estimated in the solutions by titration with titanous chloride, ferric ammonium sulphate in known quantity and potassium thiocyanate in excess being added as indicator. The method is well known and is described by Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 1918) and other workers.

A source of error, apparently hitherto unremarked, lies in the

somewhat rapid decomposition of ferric and cupric thiocyanates by water at the ordinary and at higher temperatures. These reactions were investigated by Philip and Bramley (J., 1913, **103**, 795; 1916, **109**, 597), who showed that the salts were reduced; in the case of the ferric salt, the rate of reduction was diminished by acid when an excess of alkali thiocyanate was present, and greatly increased by a rise in temperature; but the rate of reduction of cupric thiocyanate was not investigated. The results of a brief study of these sources of error, in so far as they concerned the other research, are now reported.

The titrations were carried out according to the technique described by Knecht and Hibbert, carbon dioxide being passed through the flask. A 15% solution of titanous chloride, after being boiled with concentrated hydrochloric acid, was diluted to give an approximately 0·02*N*-solution, and stored in the apparatus depicted (*loc. cit.*). (The diluted solution contained as impurity about 0·00013 g. of iron per c.c. as determined by oxidising 5 c.c. of the original 15% solution with acidified potassium permanganate and titrating the resulting ferric salt with a standardised titanous chloride solution.) A solution of standardised (approx. 0·025*N*) acidified ferric ammonium sulphate was used for checking the titanous chloride solution before and after each series of titrations, a slight but continuous decline in strength being noted.

Decomposition of Ferric Thiocyanate.—Solutions of ferric thiocyanate, prepared by mixing 25 c.c. of ferric chloride solution of known strength with 10 c.c. of 10% potassium thiocyanate (A.R.), containing different quantities of hydrochloric acid were titrated with standard titanous chloride at various intervals after mixing. The results (Table I) show that the decomposition is slight at the

TABLE I.

Conc. of $Fe(CNS)_3$, *N*.	Acidity due to added HCl, *N*.	Temp.	Interval between mixing and titration (mins.).	Ferric salt reduced, %.
0·0184	nil	16°	3	<0·2
			6	0·5
			10	0·5
0·0184	nil	25	6	1·4
0·0189	nil	50	*ca.* 0·5	4·7
			1·5	11·5
			3	16·1
0·0189	0·43	50	*ca.* 0·5	1·7
			1·5	8·4
			3	12·9
*0·155	nil	25	12	5·1
			46	7·5
*0·155	0·25 (H_2SO_4)	25	15	2·5
			50	3·6

* Experiments by Philip and Bramley.

ordinary temperature, and (in agreement with Philip and Bramley) that it is more pronounced at higher temperatures, but is inhibited by acid. Consequently, in analytical work the titration of ferric thiocyanate solutions must be carried out at the ordinary temperature in the presence of free acid and without undue delay after addition of thiocyanate to the ferric salt.

Decomposition of Cupric Thiocyanate.—Titrations with titanous chloride after different intervals were made on portions of 25 c.c. of cupric chloride solution (A.R.) to which had been added as indicator 10 c.c. of 10% potassium thiocyanate (A.R.) and 5 c.c. of the standard ferric solution together with varying amounts of hydrochloric acid. Typical results are given in Table II.

TABLE II.

Conc. of $Cu(CNS)_2$, *N*.	Acidity due to added HCl, *N*.	Temp.	Interval between mixing and titration (mins.).	Cupric salt reduced, %.*
0·0151	Nil	16°	*ca.* ½	3·8
			2	6·6
			4	8·0
0·0144	0·09	Room temp.	2	<0·1
			6	0·7
0·0151	*ca.* 1·2	Room temp.	2½	0·2
			71	1·3

* Since the velocity of change of ferric thiocyanate at the ordinary temperature is seen to be small compared with that of cupric thiocyanate, the total reduction has been ascribed to the latter.

Solutions of cupric chloride containing hydrochloric acid in concentrations from 0·25*N* to 3·3*N*, when titrated at the ordinary temperature with titanous chloride as soon as possible after addition of potassium thiocyanate, gave results which agreed amongst themselves within 0·1%. It is thus seen to be essential in the titration of cupric thiocyanate solutions to observe the same precautions as in the case of ferric thiocyanate.

When solutions of cupric chloride (*ca.* 0·015*N*) and 10% potassium thiocyanate (with or without added acid) were mixed and kept for 10 minutes or more before titration with titanous chloride, sharp end-points were not obtained; after the red colour of the ferric thiocyanate indicator had yielded to a colourless solution holding a pale grey precipitate, it developed again in a few seconds. Further addition of a drop of titanous chloride caused decoloration followed by renewed appearance of colour, and so on. The phenomenon is ascribed to the precipitation of cupric thiocyanate from the solution while awaiting titration, black acicular crystals having been observed under such conditions; in the course of the titration the precipitate slowly redissolves and reacts at the end to re-form ferric thiocyanate.

This supplies another reason why titration of cupric thiocyanate solutions should be done without loss of time.

By following Knecht and Hibbert's method with the addition of the precautions mentioned, analyses with an error of less than 0·2% were easily obtained. The titanous chloride solutions were standardised against a solution of cupric chloride (A.R.) in which the chlorine had been determined gravimetrically as silver chloride and/or the copper as cuprous thiocyanate.

A more convenient method of preparing a standard copper solution consists in dissolving a known weight of electrolytic copper in a solution of sodium peroxide in hydrochloric acid. About 5 g. of sodium peroxide are added to about 20 c.c. water and the solution is acidified with concentrated hydrochloric acid, being kept cool meanwhile. About 1 g. of pure copper turnings is added and dissolves in about ½ hour. The solution is then boiled under reflux to decompose all hydrogen peroxide (or to drive off dissolved chlorine), and diluted to a convenient volume. This method gave results from 0·1 to 0·2% lower than that previously described, probably on account of the presence of traces of iron in the sodium peroxide used.

The use of ferrous ammonium sulphate as a primary standard has been adversely criticised by the U.S. Bureau of Standards (Circular No. 26, 1921, 11) and by Thornton and Wood (*Ind. Eng. Chem.*, 1927, **19**, 150), and the author's results are in agreement with this.

The reduction of solutions of cupric thiocyanate on standing gives a ready explanation of Tomiček's observation (*Rec. trav. chim.*, 1924, **43**, 798) that when copper sulphate solutions were titrated by the potentiometric method in the presence of an excess of potassium thiocyanate large divergences from the expected figures were obtained; his suggestion that the thiocyanate is changed to sulphide, the copper salt being thereby fixed, is probably incorrect.

Highly erratic results were also recorded by Mach and Lederle (*Landw. Versuchs-Stat.*, 1914, **84**, 142) when titrating mixtures of ferric chloride and cupric sulphate in the presence of potassium thiocyanate, the ascertained copper content of cupric sulphate crystals varying from 25·08 to 18·26% with increasing concentration of ferric salt, whilst analysis by the electrolytic method gave 25·52% copper. These vagaries may perhaps also be ascribed to decomposition of the thiocyanates prior to titration, or alternatively to precipitation of cupric thiocyanate from the solutions.

The author desires to express his indebtedness to Dr. S. R. Carter for valuable assistance in the course of the work.

THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCLXXII.—*Studies of Equilibria in the Systems Sodium Chloride–Lead Chloride–Water, Lithium Chloride–Lead Chloride–Water.*

By GEORGE E. R. DEACON.

THE purpose of this work was the investigation of those complex salts, if any, formed by lead chloride with sodium or lithium chloride, which are capable of existence in contact with aqueous solutions at 25°, and to obtain the isothermal diagrams for these systems.

The method used was the same as that described by Burrage

FIG. 1.

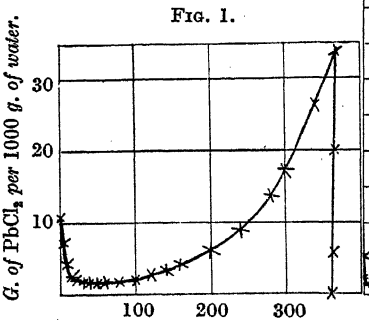
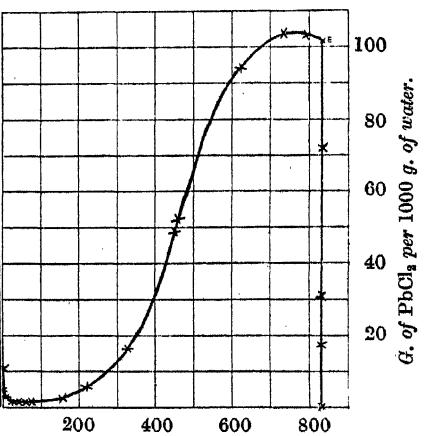


FIG. 2.



(J., 1926, 1703). The lead was estimated gravimetrically as chromate and the total chloride as silver chloride, water being found by difference. The analytical results for the liquid and wet solid phases were plotted on triangular diagrams according to Schreinemakers's method of residues; they exhibit the nature of the results more clearly, however, when plotted as in Figs. 1 and 2.

Lead Chloride–Sodium Chloride–Water.

Previous work on this system has led to conflicting results. (Mme.) Demassieux (*Ann. Chim.*, 1923, **20**, 233) studied the system at 100°, 50°, and 13°, and found that no double compounds existed. Kendall and Sloan (*J. Amer. Chem. Soc.*, 1925, **47**, 2306), working at 25°, describe the compound $2PbCl_2,NaCl$. The present investigation shows the absence of any such compound, the solid phases being lead chloride and sodium chloride only.

TABLE I (see Fig. 1).

Composition of the equilibrium solutions at 25° for the system $NaCl$–$PbCl_2$–H_2O. (Concentrations are expressed as g. per 1000 g. of water.)

NaCl.	$PbCl_2$.	Solid phase.	NaCl.	$PbCl_2$.	Solid phase.
—	10·87	$PbCl_2$.	143·0	3·52	$PbCl_2$.
5·0	7·24	,,	160·0	4·14	,,
8·8	4·22	,,	200·0	6·01	,,
15·57	2·52	,,	240·0	8·87	,,
20·0	2·09	,,	280·0	13·77	,,
30·0	1·80	,,	300·0	17·30	,,
40·0	1·72	,,	320·0	21·50	,,
50·0	1·67	,,	340·0	26·40	,,
60·0	1·75	,,	369·9	34·80	$PbCl_2$ + NaCl.
80·0	1·88	,,	367·0	20·10	NaCl.
100·0	2·14	,,	363·0	8·20	,,
121·0	2·79	,,	359·6	—	,,

Lead Chloride–Lithium Chloride–Water.

This system has been investigated at 50° by Demassieux (*loc. cit.*), and some measurements have also been made at 25° by Kendall and Sloan (*loc. cit.*), who claimed the existence of the salt $LiCl,2PbCl_2$. The present work shows the absence of this salt at 25°, and that of Demassieux shows that no compound is formed at 50°.

The system is singular in that the decrease in solubility of the lead chloride to 1·39 g. and the subsequent increase to 103·5 g. are followed by a slight decrease in solubility to 101·6 g. before the eutectic point is reached. The curve undergoes a break at the eutectic point, and a second solid phase $LiCl,H_2O$ separates. The separation of the monohydrate is in agreement with the work of Bogorodsky (*J. Russ. Phys. Chem. Soc.*, 1893, **25**, 316), who describes this hydrate as the stable form between 12·5° and 98°.

TABLE II (see Fig. 2).

Composition of equilibrium solutions at 25° for the system $LiCl$–$PbCl_2$–H_2O. (Concentrations are expressed as g. per 1000 g. of water.)

LiCl.	$PbCl_2$.	Solid phase.	LiCl.	$PbCl_2$.	Solid phase.
—	10·87	$PbCl_2$.	257·7	8·02	$PbCl_2$.
3·88	4·74	,,	329·2	16·36	,,
6·67	2·68	,,	453·9	48·71	,,
7·16	2·58	,,	458·8	52·34	,,
20·24	1·67	,,	621·8	94·43	,,
21·64	1·58	,,	735·2	103·5	,,
29·74	1·53	,,	794·1	103·4	,,
43·77	1·39	,,	834·9	101·6	$PbCl_2$ + $LiCl,H_2O$.
59·94	1·52	,,	835·0	72·0	$LiCl,H_2O$.
75·88	1·53	,,	835·0	31·0	,,
156·2	2·58	,,	830·0	17·2	,,
221·6	5·61	,,	830·5	—	,,

Treis (*Jahrb. Min. Beil.-Bd.*, 1914, **37**, 766), investigating the binary systems $PbCl_2$–XCl (where X = Li, Na, K, or Rb), found that whilst potassium gave two double compounds, and rubidium three, no combination was obtained between lithium or sodium chloride and lead chloride. Double salts are also formed between potassium and lead chlorides in aqueous solution (Burrage, *loc. cit.*).

Summary.

1. Equilibria existing at 25° in the systems NaCl–$PbCl_2$–H_2O, and LiCl–$PbCl_2$–H_2O have been investigated over the whole range of concentrations.

2. At this temperature, no double salts are capable of existence in either system.

The author desires to thank Professor Allmand, under whose direction this work was carried out during the session 1926—1927.

UNIVERSITY OF LONDON,
KING'S COLLEGE. [*Received, July 9th*, 1927.]

CCLXXIII.—*Ferric Thiocyanate.*

By KENNETH CLAUDE BAILEY.

IT is generally assumed that the blood-red substance produced by the interaction of ferric chloride and potassium thiocyanate, and extracted by ether from its aqueous solution, is ferric thiocyanate. Kruss and Moraht (*Ber.*, 1889, **22**, 2054) obtained double salts, to which they attributed the formulæ $9KSCN,Fe(SCN)_3,4H_2O$ and $3KSCN,Fe(SCN)_3,nH_2O$, by crystallisation from aqueous mixtures, but these salts were decomposed by moist ether, and could not account for the colour extracted by that solvent.

Clarens's suggestion (*Bull. Soc. chim.*, 1923, **33**, 988) that the substance obtained in presence of an excess of ferric chloride is a dithiocyanate has been combated by the author (*Proc. Roy. Irish Acad.*, 1924, **37**, *B*, 2, 6).

Tarugi stated (*Gazzetta*, 1904, **34**, ii, 326; *Annali Chim. Appl.*, 1925, **15**, 416; 1926, **16**, 281) that the red compound was a per oxidised ferrous salt, $FeHC_3N_3S_3O_3$, but his conclusions from hi earlier work were disputed by Bongiovanni (*Gazzetta*, 1907, **37**, i, 472). Although Tarugi reaffirmed these conclusions in his later work, it was deemed desirable to repeat his experiments and examine point by point the most striking arguments which he adduced in support of his formula.

According to his directions, therefore, an excess of freshly prepared ferric hydroxide was dissolved in aqueous thiocyanic acid, the solution saturated with sodium chloride and extracted with ether, and the extract filtered and dried, where desirable, over anhydrous sodium sulphate. The results obtained were identical with those given by an ethereal extract of ferric chloride and potassium thiocyanate (excess).

(1) A little of the fresh ethereal solution was added to water, and then gave a deep blue colour with potassium ferrocyanide and only a yellow colour with ferricyanide (Tarugi obtained a greenish colour and a blue colour, respectively). After being kept for some time, the solution gave a blue colour with ferricyanide, showing slow reduction of part of the iron to the ferrous condition.

(2) When dilute nitric acid was added to a strong solution of potassium thiocyanate, and the mixture shaken with ether, a red extract was obtained which was strongly acid. This result can hardly be attributed to oxidation as asserted by Tarugi, for a similar extract was obtained when hydrochloric acid was substituted for nitric acid, and the substance extracted was almost certainly thiocyanic acid (compare Bailey, *loc. cit.*; Werner and Bailey, J., 1926, 2970).

(3) A solution of ferric sulphate was prepared containing 5·58 g. per litre of iron and excess of acid. If no excess acidity had been present, 30 c.c. of $N/10$-sodium hydroxide should have sufficed to precipitate all the iron in 10 c.c. and give a neutral solution. About 69 c.c. were actually needed; 10 c.c. of the ferric solution contained, therefore, the equivalent of about 39 c.c. of $N/10$-acid in excess. When similar titrations were performed with solutions containing potassium thiocyanate and potassium oxalate, very indefinite results were obtained by the use of phenolphthalein, the indicator employed by Tarugi. Neutral litmus paper gave consistent results and was employed throughout.

Another source of error lay in the fact that the iron was not completely precipitated from solutions containing thiocyanate and oxalate until a fair excess of alkali was present, and there was a danger of adsorption of the alkali by the precipitated hydroxide. To avoid this, the solution was boiled, and 68 c.c. of $N/10$-alkali were added. The solution was filtered, the filter-paper washed, and further alkali added to ensure complete precipitation. The solution was again filtered, and the solution and washings were back-titrated with $N/10$-sulphuric acid. This procedure was followed even in the case of the plain ferric sulphate solution, to ensure uniformity of results, for each filtration necessarily incurs loss. The following results were obtained:

10 C.c. of ferric sulphate solution required 69·1 c.c. of $N/10$-sodium hydroxide.

10 C.c. of ferric sulphate solution + 60 c.c. of $N/10$-potassium thiocyanate (*i.e.*, 6 mols.) required 69·3 c.c.

10 C.c. of ferric sulphate solution + excess of concentrated potassium thiocyanate + potassium oxalate until solution was pale yellow required 69·1 c.c.

No increase in free acidity due to the reduction of iron to the ferrous condition was observed, and the only plausible explanation of Tarugi's statement, that such increase occurs, is that an error was introduced by the use of phenolphthalein, or by adsorption of sodium hydroxide by the precipitate.

Tarugi suggested that the decolorisation of the red solution by potassium oxalate was due to reduction of the red peroxidised compound by the oxalate. If this were the case, an amount of potassium oxalate equivalent to the original red compound should be oxidised during the reaction.

Quantitative estimations showed that no oxalate disappeared during the operation, and that twenty times as much oxalate was necessary for approximate decolorisation as should have sufficed for reduction of the peroxidised compound supposed to be present. This result was consistent with the disappearance of the red colour by double decomposition, but not with reduction of a peroxidised compound at the expense of the oxalate.

(4) Some fresh, red, ethereal solution was decolorised by potassium oxalate. Ammonia was added and the precipitate was quickly filtered off, washed with air-free water, and dissolved in hydrochloric acid; the solution gave an intense blue colour and precipitate with ferrocyanide, but only a greenish-yellow solution with ferricyanide. Tarugi's result (that the iron is precipitated in the ferrous condition) is only intelligible on the supposition that the ferric oxalate solution was exposed to sunlight, which would probably cause formation of some ferrous oxalate.

(5) Some of the ethereal solution was treated with oxalate, calcium chloride, and ammonia, as directed by Tarugi. The precipitate, as before, contained ferric iron and no ferrous iron. To the neutralised filtrate one drop of very dilute ferric chloride solution was added. A red colour, readily extracted by ether, was produced. Tarugi obtained a red colour not extracted by ether. This result may be easily explained. If the solutions employed are fairly dilute, the filtrate is a very dilute solution of thiocyanate, and even one drop of concentrated ferric chloride produces an excess of the latter reagent. The red colour is then only extracted with diffi-

culty. By using concentrated solutions of the other reagents and a dilute solution of ferric chloride, a mixture is obtained in which the thiocyanate is in excess, and the colour is readily extracted (see Durand and Bailey, *Bull. Soc. chim.*, 1923, **33**, 653; Bailey, *loc. cit.*).

(6) To water freed from air by boiling, some ammonia was added in a separating funnel, and red ethereal solution till the funnel was quite full. After shaking, the precipitate was allowed to subside, and had the typical appearance of ferric hydroxide; it was rapidly and repeatedly washed with air-free water, and dissolved in a little acid. The resulting solution gave no blue colour with ferricyanide. The supernatant liquid was tested for thiocyanate as under (5), with similar results.

(7) The ethereal solution gave a blue colour with benzidine, but a similar result was obtained with ferric chloride and benzidine. This reaction, therefore, does not prove the peroxidised nature of the red compound.

(8) An attempt was made to crystallise the red compound from its ethereal solution, dried over anhydrous sodium sulphate. This solution, however, when kept in a desiccator, changed in composition even before depositing solid, and a solution which originally gave only a yellow colour with ferricyanide soon gave a blue colour, showing conversion of iron into the ferrous state. After the solution had evaporated almost completely, the residue remained moist for about a week. This red liquid was acid in reaction, and doubtless contained free thiocyanic acid. A large proportion of the iron in the solid residue, although not all, was in the ferrous condition.

Philip and Bramley (J., 1913, **103**, 795) observed reduction of ferric thiocyanate in aqueous solution:

$$8Fe(CNS)_3 + 6H_2O = 8Fe(CNS)_2 + 7HCNS + CO_2 + H_2SO_4 + NH_3.$$

It seems possible that a similar reduction of ferric thiocyanate to ferrous thiocyanate with production of thiocyanic acid is taking place here. In view of the undoubted and rapid alteration of the red product, it seems unlikely that an analysis of any substance crystallised from the ethereal solution in a desiccator (Tarugi found Fe, 20·59; S, 34·37. Calc. for $FeHC_3N_3S_3O_3$: Fe, 20·07; S, 34·40%) can give results sufficiently trustworthy to establish a formula such as that proposed by Tarugi.

Summary.

Many of the experiments described by Tarugi have been carefully repeated. No evidence was obtained to support his conclusion that the red compound formed by dissolving ferric hydroxide in an

aqueous solution of thiocyanic acid is $FeHC_3N_3S_3O_3$. The results all indicate that the compound is ferric thiocyanate.

The author wishes to express his gratitude to Professor E. A. Werner for the helpful interest which he has taken in this work.

TRINITY COLLEGE, DUBLIN. [*Received, June 21st*, 1927.]

CCLXXIV.—*The Inflammation of Mixtures of the Paraffins and Air in a Closed Spherical Vessel.*

By GEORGE BARTON MAXWELL and RICHARD VERNON WHEELER.

IN a previous paper on the inflammation of mixtures of methane and air in a closed spherical vessel (J., 1918, **113**, 840), ignition being at the centre, it was recorded that the maximum pressures developed were about 10% less than the calculated values. For the calculations, the degree of dissociation of the products when inflammation had spread through the vessel was determined by analyses of samples rapidly withdrawn at the moment of attainment of maximum pressure; and Langen's values for specific heats were used. Close agreement between results obtained for mixtures of the same composition, inflamed within spheres of 4 and 16 litres capacity, showed that losses due to conduction of heat could not entirely account for the low experimental values, which were ascribed mainly to radiation losses. Experiments by Tizard and Pye (Empire Motor Fuels Committee, Report, 1923—24) with internal-combustion engines, gave surprisingly high results for the pressures produced on explosion of mixtures of heptane and air, the observed pressures being but little less than those calculated. Either the heat loss during the inflammation of heptane is considerably less than with methane, or the method of calculating explosion-temperatures used by Tizard and Pye gave low values.

The work herein described was undertaken to elucidate this matter and to study the factors which influence the rate of inflammation of hydrocarbons. The hydrocarbons used were the first five members of the paraffin series. Save that the pressure-gauge was fitted with a stronger spring than in the earlier determinations, the explosion-vessel (a 4-litre sphere) and the method of experiment were as described previously (*loc. cit.*). To ensure strictly comparable results throughout the series, the experiments with methane and ethane (see J., 1919, **115**, 81) were repeated. The pressures measured were slightly higher than in the earlier records, but the results, given in the tables that follow, did not otherwise differ

materially. Each table of observed results is followed by calculations of the maximum temperatures attainable and the theoretical maximum pressures for a number of mixtures. The method of calculation, which is explained in the experimental portion of the paper, was based on that used by Tizard and Pye (*loc. cit.*), whose data we have employed. The theoretical composition of the products of combustion of each mixture, and the ratios of the number of molecules present at the moment of maximum temperature to the initial number ("molecular ratios") are also recorded. All the mixtures were at an initial temperature and pressure of 15° and 1 atmosphere, and were ignited at the centre of the sphere.

TABLE I.

Mixtures of Methane and Air.

Theoretical mixture for complete combustion: 9·47% CH_4.
Approximate limits of inflammability: 5·6—13·6% CH_4.

Methane, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
6·05	0·167	0·545	2·67
6·40	0·122	0·340	3·80
7·15	0·076	0·151	5·08
7·35	0·058	0·119	5·69
8·30	0·025	0·081	6·63
8·60	0·025	0·078	6·91
9·15	0·031	0·070	7·21
9·65	0·021	0·069	7·35
9·70	0·031	0·068	7·37
10·20	0·020	0·067	7·43
10·40	0·038	0·068	7·28
10·80	0·021	0·071	7·21
11·40	0·040	0·087	6·88
11·90	0·045	0·102	6·54
12·10	0·041	0·137	6·41
12·70	0·071	0·257	5·35
13·40	0·166	0·368	4·23

Calculated Maximum Temperatures and Pressures.

CH_4, %.	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
7·00	6·70	0·17	15·40	0·05	5·46	72·22	1·0005	2005°	6·90
8·00	7·27	0·56	17·21	0·14	3·54	71·28	1·0010	2155	7·48
9·00	7·37	1·41	18·87	0·39	1·85	70·11	1·0072	2265	7·88
9·47	7·21	1·98	19·47	0·58	1·28	69·48	1·0130	2300	8·04
9·70	7·00	2·42	19·80	0·65	0·92	69·21	1·0135	2310	8·10
10·00	6·79	2·87	20·20	0·77	0·69	68·68	1·0185	2320	8·17
11·00	5·52	4·93	20·70	1·72	0·13	67·00	1·0275	2275	8·10
12·00	4·03	7·15	20·68	3·30	0·01	64·83	1·0550	2185	8·00
13·00	2·30	9·30	20·02	6·20	Trace	62·18	1·0934	2050	7·82

* CH_4 = nil.

TABLE II.

Mixtures of Ethane and Air.

Theoretical mixture for complete combustion : 5·64% C_2H_6.
Approximate limits of inflammability : 3·1—10·7% C_2H_6.

Ethane, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
4·10	0·056	0·113	6·34
4·45	—	0·097	6·70
4·90	0·039	0·076	7·36
5·15	0·035	0·066	7·39
5·55	0·030	0·055	7·62
6·15	0·024	0·050	7·87
6·30	0·024	0·052	7·94
6·75	0·029	0·056	7·81
6·95	0·034	0·060	7·89
7·50	0·037	0·083	7·42
7·60	0·051	0·088	7·35
8·20	0·078	0·172	6·94

Calculated Maximum Temperatures and Pressures.

C_2H_6, %	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
4·00	7·52	0·18	13·18	0·04	5·96	73·12	1·0269	1990°	7·04
4·80	8·34	0·84	15·24	0·17	3·48	71·93	1·0288	2210	7·88
5·20	8·37	1·51	16·20	0·26	2·43	71·23	1·0347	2280	8·18
5·80	8·05	2·83	17·38	0·57	1·17	70·00	1·0463	2350	8·51
6·00	7·79	3·42	17·68	0·76	0·86	69·49	1·0515	2355	8·59
6·20	7·54	4·01	18·06	0·85	0·52	69·02	1·0561	2350	8·61
7·00	5·69	7·00	18·37	2·23	0·05	66·66	1·0824	2280	8·57
8·00	3·27	10·58	17·94	4·41	Trace	63·80	1·1481	2110	8·50

* C_2H_6 = nil.

TABLE III.

Mixtures of Propane and Air.

Theoretical mixture for complete combustion : 4·02% C_3H_8.
Approximate limits of inflammability : 2·2—7·3% C_3H_8.

Propane, %.	Time from ignition to first appearance of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·45	0·143	0·303	4·37
3·50	0·039	0·073	7·51
3·70	0·038	0·063	7·83
4·25	0·033	0·055	8·00
4·60	0·035	0·055	8·09
5·15	0·034	0·062	7·90
5·25	0·043	0·062	7·89
5·65	0·049	0·087	7·59
6·45	0·102	0·198	6·13

Calculated Maximum Temperatures and Pressures.

C_3H_8, %.	Products of combustion * at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
2·5	7·16	0·04	11·25	0·01	7·59	73·95	1·0248	1850°	6·56
3·0	8·21	0·36	13·01	0·07	5·24	73·11	1·0317	2075	7·43
4·0	8·65	2·54	16·06	0·45	1·61	70·71	1·0551	2340	8·56
4·4	8·03	4·10	16·95	0·79	0·63	69·50	1·0693	2370	8·80
4·6	7·47	5·11	17·27	1·08	0·36	68·71	1·0790	2365	8·88
5·5	4·58	9·76	17·00	3·63	0·09	64·94	1·1345	2190	8·71
6·0	2·80	12·40	16·80	5·18	0·02	62·80	1·1813	2065	8·59

* C_3H_8 = nil.

TABLE IV.

Mixtures of Butane and Air.

Theoretical mixture for complete combustion: 3·12% C_4H_{10}.
Approximate limits of inflammability: 1·65—5·7% C_4H_{10}.

Butane, %.	Time from ignition to first appearance of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·05	0·078	0·149	5·20
2·55	0·043	0·078	7·42
3·00	0·027	0·059	8·15
3·60	0·027	0·055	8·48
3·70	0·029	0·054	8·33
3·75	0·027	0·057	8·59
4·40	0·041	0·080	7·78
4·75	0·081	0·117	7·18
4·85	0·061	0·127	7·03
5·15	0·136	0·221	5·83

Calculated Maximum Temperatures and Pressures.

C_4H_{10}, %.	Products of combustion * at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
2·0	7·55	0·10	11·19	0·02	7·19	73·95	1·0301	1905°	6·80
3·0	8·89	2·26	15·16	0·36	2·03	71·30	1·0581	2330	8·56
3·5	7·94	4·77	16·59	0·87	0·51	69·32	1·0821	2380	8·95
3·7	7·20	6·09	16·79	1·38	0·20	68·34	1·0955	2355	9·00
4·5	2·76	12·24	16·28	5·11	0·01	63·60	1·2091	2020	8·62

* C_4H_{10} = nil.

The Pressures developed.—Comparison between the observed and the calculated pressures is made in Fig. 1. Both experiment and calculation show the maximum pressure to be given in each instance by a mixture containing an excess of hydrocarbon over that required for complete combustion. The amounts of these "displacements" are recorded in Table VI, together with the observed and calculated maximum pressures and the amounts of "lost pressure" expressed as % of the calculated values.

FIG. 1.

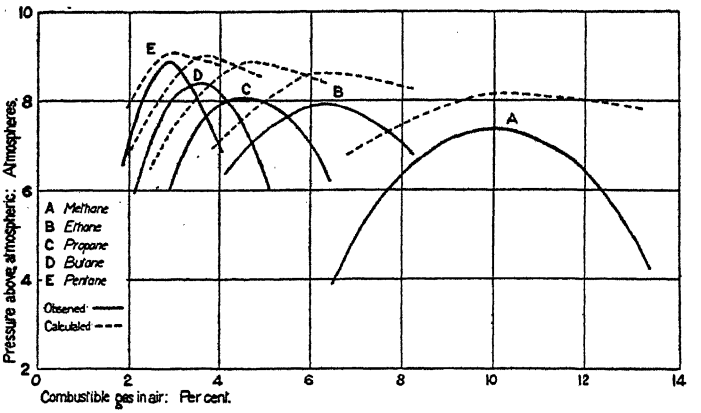


TABLE V.

Mixtures of Pentane and Air.

Theoretical mixture for complete combustion : 2·55% C_5H_{12}.
Approximate limits of inflammability : 1·35—4·5% C_5H_{12}.

Pentane, %.	Time for ignition to first appearance of press. (sec.).	Time for ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
1·95	0·057	0·110	6·65
2·05	0·056	0·089	7·54
2·30	0·045	0·071	7·80
2·40	0·044	0·069	8·10
2·70	0·038	0·059	8·74
2·80	0·024	0·056	8·93
3·00	0·030	0·059	8·87
3·15	0·033	0·064	8·77
3·45	0·037	0·065	8·09
3·60	0·063	0·099	7·91
3·85	0·076	0·021	7·58
4·10	0·113	0·191	6·97

Calculated Maximum Temperatures and Pressures.

C_5H_{12}, %.	Products of combustion * at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
2·0	8·82	0·62	12·88	0·09	4·56	73·03	1·0340	2155°	7·80
2·5	9·06	2·49	15·08	0·39	1·78	71·20	1·0645	2350	8·70
2·75	8·52	3·98	15·77	0·81	0·92	70·00	1·0799	2380	8·94
3·0	7·45	5·98	16·45	1·21	0·27	68·64	1·0985	2370	9·07
4·0	2·04	14·04	16·64	4·87	Trace	62·41	1·1959	2075	8·75

* C_5H_{12} = nil.

The close agreement in composition between the observed and calculated maximum-pressure mixtures leads to the conclusion that

TABLE VI.

Compositions of Mixtures giving Maximum Pressures. Lost Pressures, %.

	Theoretical mixture for complete combustion, %.	Mixture giving maximum press., %.		Maximum press.		Lost press., %.
		Calc.	Obs.	Calc.	Obs.	
Methane	9·47	10·00	10·00	8·18	7·38	9·80
Ethane	5·64	6·20	6·30	8·63	7·91	8·35
Propane	4·02	4·60	4·60	8·87	8·09	8·80
Butane	3·12	3·70	3·65	9·00	8·50	5·55
Pentane	2·55	3·00	2·95	9·07	8·85	2·45

the " displacements " are the effects of dissociation on the explosion-temperatures and " molecular ratios," for which allowance was made in the calculations.

The " lost pressure " may be due to loss of heat by conduction and radiation or to incomplete combustion. It was shown in a previous paper (*loc. cit.*) that, in mixtures of methane and air containing between 7·5 and 12·5% of methane, a loss of heat by conduction of 2—3% can be presumed during the attainment of uniformity of temperature after inflammation. Such a loss may be assumed also with the other hydrocarbons. It is not easy to obtain a comparison of radiation losses during combustion of each hydrocarbon from the calculated compositions of the products. The intensities of radiation from steam and from carbon dioxide have been determined by Julius (" Die Licht- und Warmestrahlung verbrannter Gase," Berlin, 1890) and R. von Helmholtz (" Die Licht- und Warmestrahlung verbrennender Gase," Berlin, 1890), but the most trustworthy figures seem to be those recorded by Haslam, Lovell, and Hunneman (*Ind. Eng. Chem.*, 1925, **17**, 272), who estimated (by measuring the radiation from flames of methane and carbon monoxide, the theoretical amount of primary air being used with each) that the intensity of radiation from steam was about 1·7 times that from carbon dioxide. If these results be accepted, a comparison can be made of the relative " radiating powers " of the mixtures of carbon dioxide and steam in the products of combustion of the different hydrocarbons. Such a comparison is made in Table VII. The figures in columns 2 and 3 give the relative numbers of molecules of carbon dioxide and steam calculated to be present in the products of combustion of each maximum-pressure mixture at the moment of maximum pressure. These values were obtained from Tables I—V by multiplying the respective volume percentages by the corresponding molecular ratio.

The radiating power thus decreases from the methane to the pentane mixture, which is in accord with the decrease in " lost

TABLE VII.

Relative Radiating Powers of Products of Combustion of Maximum-Pressure Mixtures.

Mixture.	CO_2, g.-mols.	H_2O, g.-mols.	Ratio, H_2O/CO_2.	Relative radiating power. ($CO_2\% + 1{\cdot}7\,H_2O\,\%$.)
CH_4, 10·0%	0·0691	0·2058	2·98	41·8
C_2H_6, 6·2%	0·0796	0·1907	2·40	40·3
C_3H_8, 4·6%	0·0806	0·1863	2·31	39·7
C_4H_{10}, 3·7%	0·0789	0·1838	2·33	39·1
C_5H_{12}, 3·0%	0·0818	0·1808	2·21	38·9

pressure" (Table VI). It must be borne in mind, however, that the calculated maximum explosion-temperature rises from the methane to the pentane mixture, which would offset the decreasing H_2O/CO_2 ratio because of the difference in the mean wave-lengths of the radiations. It is, on the whole, improbable that differences in radiation loss account entirely for the differences in "lost pressure."

A more probable explanation lies in errors in the values for specific heats (Bjerrum, *Z. Elektrochem.*, 1911, **17**, 731; 1912, **18**, 101) on which our calculations, as also Tizard and Pye's, were based. Recent work by Womersley (*Proc. Roy. Soc.*, 1921, *A*, **100**, 483) suggests that Bjerrum's values for steam at high temperatures were much too low. Womersley's results extend only to 2000°, and for calculations of explosion-temperatures higher than this figure extrapolated values must be used. A few calculations are recorded in Table VIII, and if they are compared with those given in Table I, it will be seen that the composition of the mixture for which the calculated pressure is greatest (10% methane) is unchanged, but that the value for the pressure, 7·59 as compared with 8·17 atm., is considerably lower when Womersley's figures are used. The calculated pressure is, in fact, very near that found

TABLE VIII.

Calculated Maximum Temperatures and Pressures on Explosion of Methane–Air Mixtures.

(Based on Womersley's values for the specific heat of steam.)

CH_4 in original mixture,	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
%.	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
9·8	7·80	1·71	20·12	0·58	0·42	69·37	1·0112	2160°	7·54
10·0	7·52	2·16	20·35	0·70	0·30	68·98	1·0145	2165	7·59
10·2	7·25	2·62	20·56	0·81	0·13	68·63	1·0174	2150	7·57

* CH_4 = nil.

experimentally (7·38 atm.). No doubt the true value for the mean specific heat of steam over the range 100—2000° lies between

Bjerrum's (8·42 cals. per g.-mol.) and Womersley's (11·69). If so, calculations of maximum explosion-temperatures based on Bjerrum's figures would be too high, and the amount of the error would increase with the amount of steam in the products of combustion. Values for the amounts of steam in the products of combustion of unit volume of the maximum-pressure mixture for each hydrocarbon at the moment of maximum pressure are given in Table VII, from which it appears that over-estimation of loss of pressure would be greatest with methane and least with pentane (see Table VI).

There may also be error in the values (from Nernst, *Z. anorg. Chem.*, 1905, **45**, 130; and Bjerrum, *Z. physikal. Chem.*, 1912, **79**, 513) used in estimating the amount of dissociation of carbon dioxide and steam. In this connexion, it is of value to compare the analyses of samples of the gases rapidly withdrawn from the explosion-vessel at the moment of maximum pressure with methane–air mixtures (J., 1918, **113**, 840) with the calculated compositions of the products of combustion of similar mixtures (Table IX).

TABLE IX.

Observed and Calculated Compositions of Products of Combustion, %.

CH_4 in original mixture,	CO_2,		CO,		H_2,		O_2,		CH_4,
%	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.*
7·90	9·25	7·21	0·15	0·49	Nil	0·11	3·82	3·72	Nil
9·40	11·14	7·20	0·26	1·96	,,	0·50	0·74	1·31	,,
9·90	10·66	6·84	1·12	2·74	0·40	0·77	0·13	0·77	0·24
10·00	10·86	6·79	1·08	2·87	0·68	0·77	0·04	0·69	0·04
10·70	9·04	5·95	3·63	4·30	2·21	1·40	Nil	0·24	0·10
11·05	9·00	5·45	3·44	5·00	1·95	1·77	,,	0·13	0·23
12·10	8·09	3·84	5·85	7·30	4·00	3·46	0·07	0·01	0·07
12·90	6·08	2·51	7·78	9·02	6·73	5·80	0·05	Nil	0·36
13·90	5·45	0·84	8·95	11·50	9·45	9·50	Nil	,,	1·00

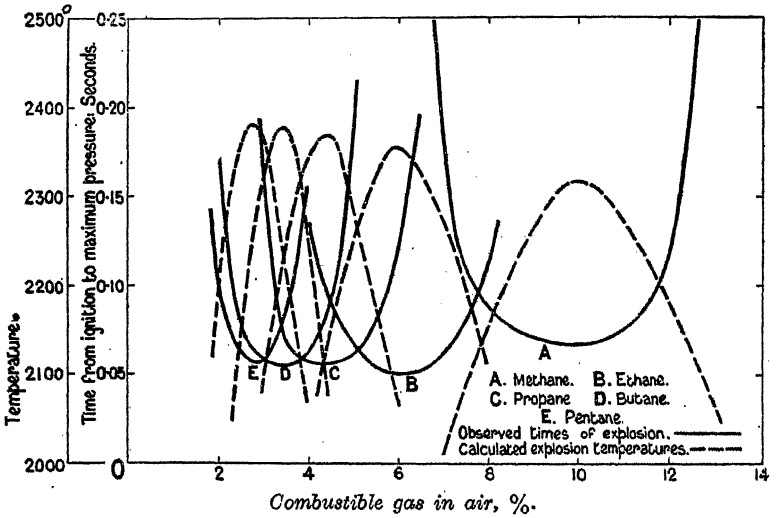
* "Calc. = nil."

There is an indication from these results that the extent of the dissociation of carbon dioxide has been over-estimated in the calculations, for the experimental values for the amounts of this gas in the products of combustion at the moment of maximum pressure are consistently high. In part, the discrepancy might be due to recombination during cooling of the samples (which was, however, very rapid), but this is not likely in view of the close agreement of the observed and calculated figures for hydrogen. Further, Fig. 1 shows that the discrepancy between observed and calculated pressures is greatest for mixtures containing an excess of combustible gas, a result which can be attributed to over-estimation of the "molecular ratios" in the calculations. It would thus seem that the decrease in "lost pressure" in passing from methane to pentane

(Table VI) may be more apparent than real. It is probable that the unexpectedly close agreement between calculated and observed engine efficiencies with heptane as fuel, recorded by Tizard and Pye, was also due to errors in the data on which the calculations were based.*

The Rate of Development of Pressure.—With a given hydrocarbon, it is apparent that the main factor controlling the mean rate of pressure development on explosion of its mixtures with air is the mean temperature of explosion. This is clear from Fig. 2, in which the effect of variation in composition of the mixtures on the rate of development of pressure is shown graphically for each hydro-

FIG. 2.



carbon, together with the calculated explosion-temperatures. Table X has been compiled from Fig. 2, and makes comparison between the observed "maximum-speed" mixtures and the calculated "maximum-temperature" mixtures. The "maximum-speed" mixture for each gas is that in which the time from ignition to the attainment of maximum pressure is least.

As a corollary to the observation that, under the conditions of these experiments, the mean rate of pressure development with a given paraffin is determined by the mean explosion-temperature, it follows that the "displacement" of the maximum-speed mixture

* Fenning and Tizard have recently published a paper on the dissociation of carbon dioxide at high temperatures (*Proc. Roy. Soc.*, 1927, *A*, **115**, 318) which confirms our conclusion. (Added July 10th, 1927.)

TABLE X.

Composition of Maximum-speed and Maximum-temperature Mixtures.

	Hydrocarbon in maximum-speed mixture (obs.), %.	Hydrocarbon in maximum-temperature mixture (calc.), %.	Mean temp. (calc.).	Time (obs.) from ignition to maximum-pressure (sec.).
Methane	10·0	10·0	2320°	0·067
Ethane	6·05	6·0	2355	0·051
Propane	4·45	4·4	2370	0·055
Butane	3·50	3·45	2380	0·055
Pentane	2·90	2·8	2380	0·057

is due to the same cause, dissociation, as displaces the calculated maximum-temperature mixture.

In this connexion, it is of interest to compare the results recorded in Table X with Mason's determinations (J., 1923, **123**, 210) regarding the mixture of each of the paraffins with air which gave the maximum speed of uniform movement of flame. Mason's results are summarised in Table XI. There is general agreement between the compositions of the maximum-speed mixtures under the two

TABLE XI.

Uniform Movement in Paraffin–Air Mixtures.

	Maximum-speed Mixtures. (Mason.)	
Paraffin.	Maximum-speed mixture, %.	Speed of uniform movement (5-cm. diam. tube) (cm. per sec.).
Methane	9·65	91
Ethane	6·05	127
Propane	4·45	114
Butane	3·65	113
Pentane	2·90	115

different conditions of experiment, and the order of speed of flame in the series of mixtures is the same. This is in accord with our recent observation (this vol., p. 297) that the generalisation known as " the law of speeds," first formulated with respect to the uniform movement of flame, applies also to the rate of spread of flame within a closed sphere.

EXPERIMENTAL.

The explosion-vessel and its fittings have been described in J., 1918, **113**, 854. Ignition of the mixtures was at the centre of the vessel by a secondary discharge from a " 10-inch " induction-coil at a 1 cm. gap between pointed copper electrodes, the current through the primary circuit being 10 amps. and the trembler of the coil being locked.

The pressure-gauge was calibrated by compressed air at intervals during the series of experiments against a standard Bourdon gauge. The mean of the calibrations, which checked well amongst themselves, showed a deflexion of the manometer stylus of 1 cm. for a pressure increase of 7·85 atm.

The hydrocarbons were obtained as follows: Methane, from a blower of fire-damp in S. Wales; ethane, (*a*) by the action of water on zinc ethyl, or (*b*) from a cylinder of the compressed gas obtained (from America) by the fractionation of natural gas; propane and butane, by the action of the zinc–copper couple on the corresponding alkyl iodide in alcoholic solution; pentane, from a petroleum distillate, b. p. 35—40°. Each gas, after purification by washing with suitable solvents, was twice liquefied, the middle-boiling fraction only being retained. The ratios C/A (C = contraction on explosion analysis; A = subsequent absorption by potassium hydroxide solution) were: Methane, 1·995; ethane, (*a*) 1·253, and (*b*) 1·245; propane, 1·003; butane, 0·878; pentane, 0·804.

Each gas mixture was prepared in a 20-litre glass gas-holder over a dilute solution of potassium hydroxide and was analysed before use. Before an experiment, the explosion-vessel was exhausted of air to within a few mm. of mercury, filled with the mixture required, re-exhausted and filled again.

Calculation of Explosion Temperatures and Pressures.—The explosive mixtures were assumed to be saturated with water vapour at 15° and the analyses (which take no account of water vapour) were adjusted accordingly. The analytical figures were then proportional to the numbers of molecules of each constituent present in unit volume, and to their partial pressures.

In unit volume of the products of explosion, the numbers of molecules of the constituents can be expressed by $a\ CO_2 + b\ CO + c\ H_2O + d\ H_2 + e\ O_2 + f\ N_2$.

The ratio of the total number of molecules per unit volume at the moment of maximum temperature to the total number in unit volume of the original mixture (the "molecular ratio," M) is $(a + b + c + d + e + f)/1$. The partial pressure of, say, carbon dioxide at the moment of maximum temperature is aP_e/M, whilst $P_e = MT_e/T_i$, where P_e is the explosion-pressure in atmospheres, and T_e and T_i are the explosion-temperature and the initial temperature in °K. For example, in a mixture of pentane and air containing in unit volume: C_5H_{12}, 0·0246; O_2, 0·2005; H_2O, 0·0170; N_2, 0·7579, there are only five unknowns, for the number of molecules of nitrogen, f, can be regarded as remaining constant. Five independent relationships are therefore required to determine them. By equating the carbon, oxygen, and hydro-

gen before and after explosion, the following relationships are obtained:

$$a + b = 5 \times 0{\cdot}0246 = 0{\cdot}1230 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$2a + b + c + 2e = 2 \times 0{\cdot}2005 + 0{\cdot}0170 = 0{\cdot}418 \quad . \quad \text{(ii)}$$

$$c + d \qquad = 6 \times 0{\cdot}0246 + 0{\cdot}0170 = 0{\cdot}1646 \; . \quad \text{(iii)}$$

The equilibrium constants, K_1 and K_2, can be obtained from Nernst's data, thus:

$$K_1 = \frac{P^2_{CO} \times P_{O_2}}{P^2_{CO_2}} = \frac{b^2 e}{a^2} \cdot \frac{T_e}{T_i}; \text{ whence } \frac{b^2}{a^2} e = K_1 \frac{T_i}{T_e} \quad . \quad . \quad \text{(iv)}$$

$$\text{and } K_2 = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} = \frac{bc}{ad}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

Expressions (iv) and (v) involve the explosion-temperature, T_e. A value for this is assumed and the equations are then solved. The simplest method of solution is to attribute different values to one of the unknowns, say e, until the relationship $bc/ad = K_2$ is satisfied.

From the solutions of the equations the rise in temperature can be calculated, since it represents the ratio between the thermal energy released on explosion of unit volume of the mixture and the thermal capacity of the products of explosion of unit volume. In the pentane–air mixture chosen as an example, the thermal energy released is that from 0·0246 g.-mol. of pentane less the calorific value of b g.-mol. of carbon monoxide and d g.-mol. of hydrogen. The thermal capacity of the products = amount of each constituent multiplied by its mean specific heat between 15° and the assumed explosion-temperature.

If the explosion-temperature so calculated does not agree within 5° of the predicted value, a fresh calculation is made with a new value for T_e. In the example given, the value for T_e finally chosen was 2618° K. and the calculated value then was 2623° K. The latter was accordingly taken as representing the maximum explosion-temperature. The molecular ratio was found to be 1·0645, so that the explosion-pressure, P_e, was $(2623/288) \times 1{\cdot}0645 = 9{\cdot}7$ atm. The pressure rise above atmospheric was therefore 8·70 atm.

The experiments described in this paper have been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD.

[*Received, May 11th*, 1927.]

CCLXXV.—*The Reduction of Nitro-compounds by Aromatic Ketols. Part I. Some* p-*Azoxy-compounds.*

By HUGH BRYAN NISBET.

THAT benzoin and its analogues may reduce Fehling's solution has been known for a long time, but the possibility of reducing nitro-groups by means of these agents has not hitherto been investigated. It has now been found that benzoin, anisoin, and furoin, in hot alcoholic solution in the presence of a trace of sodium methoxide or ethoxide, may be successfully used for the reduction of nitro-groups to azoxy-groups :

$$2R{\cdot}NO_2 + 3R{\cdot}CH(OH){\cdot}CO{\cdot}R = R_2N_2O + 3R{\cdot}CO{\cdot}CO{\cdot}R + 3H_2O.$$

The reduction is particularly successful in the case of *p*-nitro-compounds such as the *p*-nitrobenzylideneanilines, *p*-nitrobenzonitrile, the *p*-nitrocinnamic esters, and the *p*-nitrostilbenes, since the azoxy-compounds formed are, in general, sparingly soluble substances and may be readily separated from the 1 : 2-diketone to which the ketol is oxidised in the course of the reaction. The reduction proceeds very quickly, in some cases with ebullition of the solvent, and in a very short time the *p*-azoxy-compounds separate from solution. The 1 : 2-diketone may be recovered in each case from the mother-liquor.

With benzoin as reducing agent, 60—70% yields of *p*-azoxybenzylideneanilines can be obtained from the corresponding *p*-nitrobenzylideneanilines. *p*-Azoxybenzylideneaniline so obtained is identical with that obtained by reducing *p*-nitrobenzylideneaniline with alkali sulphides (*Chem. Zentr.*, 1900, ii, 612) or with alcoholic potash (Alway, *Ber.*, 1902, **35**, 2436), by treating *p*-nitrobenzyl chloride with caustic potash (Alway, *loc. cit.*), or by condensing *p*-azoxybenzaldehyde with aniline (Alway, *Amer. Chem. J.*, 1902, **28**, 43). *p*-Azoxybenzylidene-*p*-toluidine prepared by this method is identical with the compound prepared by reducing *p*-nitrobenzylidene-*p*-toluidine with alkali sulphides (*Chem. Zentr.*, 1900, ii, 612) or by the condensation of *p*-azoxybenzaldehyde with *p*-toluidine (Alway, *Ber.*, 1902, **35**, 2437). *p*-Nitrobenzylidene-*p*-aminoacetophenone is reduced by benzoin to *p*-azoxybenzylidene-*p*-aminoacetophenone.

Japp and Miller (J., 1893, **63**, 474) showed that benzoin and benzonitrile in the presence of concentrated sulphuric acid condense to form triphenyloxazole ; but *p*-nitrobenzonitrile is reduced by benzoin to *p*-azoxybenzonitrile.

By this method of reduction the esters of *p*-azoxycinnamic acid can be prepared directly from the esters of *p*-nitrocinnamic acid.

and the azoxy-acid can be obtained by hydrolysis. The yields of the reduction products are good, usually 70%, and the reaction proceeds very quickly, whereas the reduction of the nitro-acid electrolytically (Marie, *Comp. rend.*, 1905, **140**, 1248) or by sodium arsenite (Vorländer, *Ber.*, 1906, **39**, 806) and the formation of the esters of the azoxy-acid through the silver salt (Vorländer, *loc. cit.*) are all tedious methods.

p-Nitrostilbenes also are easily reduced by this method to *p*-azoxystilbenes, which may be obtained in excellent yield. The table gives the *p*-azoxystilbenes prepared by this method, the approximate yield, usually the average of two experiments, and the molecular weights of those compounds which are sufficiently soluble in 2 : 4-dinitrotoluene to allow of the determination by the cryoscopic method in that solvent (Auwers, *Z. physikal. Chem.*, 1899, **30**, 310).

Azoxy-compounds.	Yield.	*M*, found.	*M*, calc.
p-Azoxystilbene	70%	396	402
p-Azoxy-2-nitrostilbene	70%	487	492
p-Azoxy-2 : 3′-dinitrostilbene	45%	—	—
p-Azoxy-2 : 6-dinitrostilbene	Small	—	—
p-Azoxy-2-nitro-4′-methoxystilbene	70%	512	552
p-Azoxy-2-nitro-3′ : 4′-methylenedioxystilbene	65%	586	580
p-Azoxy-2 : 6-dinitro-4′-methoxystilbene	45%	—	—
p-Azoxy-2-nitro-4′-dimethylaminostilbene	42%	—	—

Anisoin and furoin were substituted for benzoin in the reduction of 2 : 4-dinitrostilbene and gave approximately the same yield of the same azoxy-compound. The mother-liquors yielded anisil and furil, respectively. In all the reductions in which benzoin was used, benzil was recovered from the mother-liquors.

Experimental.

Preparation of Nitrostilbenes.—A modification of Bishop and Brady's method (J., 1922, **121**, 2367) was used. A solution of the polynitrotoluene and the aromatic aldehyde in molecular proportion and 1 c.c. of piperidine in a small quantity of benzene is boiled under reflux until the reaction is complete, the time varying from 1 to 6 hours. The benzene is then allowed to evaporate and the crystalline mass is washed with benzene–light petroleum and recrystallised from glacial acetic acid. 2 : 4-Dinitro-4′-methoxystilbene, 75% yield, m. p. 163° (compare Pfeiffer, *Annalen*, 1916, **411**, 91). 2 : 4 : 3′-Trinitrostilbene, 50% yield, m. p. 182—183° (compare Pfeiffer, *loc. cit.*). 2 : 4 : 4′-*Trinitrostilbene*, from 2 : 4-dinitrotoluene (9 g.) and *p*-nitrobenzaldehyde (7·5 g.). Yield, 12 g. Dark orange needles, m. p. 234—235° (Found : C, 53·9; H, 3·0. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). 2 : 4-*Dinitro*-3′ : 4′-*methylenedioxystilbene* from 2 : 4-dinitrotoluene (9 g.) and piperonal

(7·5 g.). Yield, 12 g. Orange-red, squat crystals, m. p. 178—180° (Found: C, 56·9; H, 3·3. $C_{15}H_{10}O_6N_2$ requires C, 57·3; H, 3·2%). 2 : 4 : 6-*Trinitro-4'-methoxystilbene*, from 2 : 4 : 6-trinitrotoluene (11 g.) and anisaldehyde (7 g.). Yield, 9·3 g. Brown needles, m. p. 167—168° (Found: C, 51·8; H, 3·3. $C_{15}H_{11}O_7N_3$ requires C, 52·2; H, 3·2%). 2 : 4-*Dinitro-4'-dimethylaminostilbene*, from 2 : 4-dinitrotoluene (9 g.) and *p*-dimethylaminobenzaldehyde (7 g.). Yield, 11 g. Small, black, lustrous plates, m. p. 181° (Found: N, 12·8. $C_{16}H_{15}O_4N_3$ requires N, 12·8%). The base forms a *chloroplatinate*, yellowish-brown needles, m. p. 211° [Found: Pt, 18·8. $(C_{16}H_{15}O_4N_3)_2,H_2PtCl_6$ requires Pt, 18·9%].

Preparation of Azoxy-compounds. General Method and Remarks.—The nitro-compound is dissolved in the smallest possible quantity of boiling alcohol, sufficient ketol for the reduction of somewhat less than the whole of the nitro-compound is added, and then a few drops of 6% alcoholic sodium methoxide or ethoxide. The solution goes dark, but soon begins to clear and a yellow or an orange precipitate settles out. After cooling a little, this is collected, dried, and recrystallised from xylene. The azoxy-compounds so obtained are, in general, yellow or bronze-yellow, and are very slightly soluble in the common solvents, slightly soluble in boiling xylene, and more soluble in boiling pyridine. If too much reducing agent be added, the reduction products are sometimes red, probably due to the formation of traces of azo-compounds.

The constitutions of the *p*-azoxystilbenes follow from the analytical figures and the molecular-weight determinations, and from their analogy to the other compounds described in this paper. That it is the *p*-nitro-group which is reduced in stilbenes containing more than one nitro-group may be safely assumed, since it has been proved already that other alkaline reducing agents, *e.g.*, ammonium sulphide, attack the *p*-nitro-group first (Thiele and Escales, *Ber.*, 1901, **34**, 2846). The insolubility of the *p*-azoxystilbenes which have been prepared so far by this method has rendered the examination of further reduction products impossible.

p-*Azoxybenzylideneaniline*, $(C_6H_5{\cdot}N{:}CH{\cdot}C_6H_4)_2N_2O$. *p*-Nitrobenzylideneaniline (8 g.) and benzoin (8 g.) gave an almost immediate separation of yellow flakes which, recrystallised from xylene, sintered at 185° and melted and decomposed at 226°. Yield, 5 g. (Found: C, 77·2; H, 5·2; N, 13·8. Calc.: C, 77·2; H, 4·95; N, 13·8%). The compound was completely identified by treating it with 27% nitric acid; *p*-azoxybenzaldehyde, m. p. 190°, and aniline were obtained (compare Alway, *Amer. Chem. J.*, 1902, **28**, 43). The *p*-azoxybenzaldehyde recondensed with aniline to give *p*-azoxybenzylideneaniline which, when mixed with the product

obtained by using benzoin as reducing agent, did not alter its melting point.

p-*Azoxybenzylidene*-p-*toluidine*, $(C_7H_7N{:}CH{\cdot}C_6H_4)_2N_2O$. *p*-Nitrobenzylidene-*p*-toluidine (2·5 g.) and benzoin (2·1 g.) gave an immediate separation of yellow flakes, which were recrystallised from boiling xylene. M.p. 217° (decomp.; sintering at 189—190°). Yield, 1·7 g. (Found: C, 77·9; H, 5·9; N, 12·5. Calc.: C, 77·7; H, 5·55; N, 12·9%).

p-*Azoxybenzylidene*-p-*aminoacetophenone*,

$$(CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_4)_2N_2O.$$

p-Nitrobenzylidene-*p*-aminoacetophenone (2·7 g.) and benzoin (2·1 g.) gave an immediate separation of yellow flakes. Recrystallised from xylene, the substance sintered at 187° and melted and decomposed at 217°. Yield, 1·8 g. (Found: C, 73·4; H, 5·15; N, 11·3; *M*, cryoscopic in 2 : 4-dinitrotoluene, 486. $C_{30}H_{24}O_3N_4$ requires C, 73·8; H, 4·9; N, 11·6%; *M*, 488).

p-*Azoxybenzonitrile*.—*p*-Nitrobenzonitrile was prepared by Sandmeyer's method (*Ber.*, 1885, **18**, 1492), but was isolated, not by sublimation, but by extracting the cuprocyanide reaction mixture several times with much boiling water; it was deposited in flakes on cooling and recrystallised from alcohol (yield, 8·2 g. from 13·8 g. of *p*-nitroaniline).

p-Nitrobenzonitrile (6 g.) and benzoin (8·5 g.) were dissolved in 100 c.c. of alcohol, and a few drops of 6% alcoholic sodium ethoxide added. p-*Azoxybenzonitrile* soon began to separate and after cooling it was collected and recrystallised from boiling toluene (yield, 5 g.); m. p. 221° (Found: C, 67·9; H, 3·5; N, 22·5; *M*, cryoscopic in 2 : 4-dinitrotoluene, 247. $C_{14}H_8ON_4$ requires C, 67·7; H, 3·2; N, 22·5%; *M*, 248).

Esters of p-*azoxycinnamic acid*. Ethyl *p*-nitrocinnamate (3 g.) and benzoin (3 g.) gave ethyl *p*-azoxycinnamate (2·1 g.), which crystallised from xylene in yellow, flocculent needles, m. p. 240°, sintering at 140° (Found: C, 67·1; H, 5·5; N, 7·1. Calc.: C, 67·1; H, 5·5; N, 7·2%).

Methyl *p*-nitrocinnamate (2 g.) and benzoin (2 g.) gave 1·4 g. of methyl *p*-azoxycinnamate, which crystallised from xylene in yellow, flocculent needles, m. p. 246°, sintering at 220° (Found: C, 65·8; H, 4·8; N, 7·35. Calc.: C, 65·6; H, 4·9; N, 7·6%).

p-Azoxycinnamic acid was obtained, by hydrolysis of either of the esters, as a yellow, amorphous solid insoluble in the common organic solvents but soluble in alkali; it decomposed at a high temperature (Found: C, 64·2; H, 4·3; N, 7·8. Calc.: C, 63·9; H, 4·1; N, 8·2%).

p-*Azoxystilbene*, $(C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_4)_2N_2O$. 4-Nitrostilbene (1·7 g.)

and benzoin (1·6 g.), treated according to the general method, gave a green solution which in a short time turned yellow and deposited a yellow, flocculent precipitate. This, after recrystallisation from xylene, sintered at 259° and melted and decomposed at 271—272° (Found: C, 83·2; H, 5·6; N, 6·9; *M*, 396. $C_{28}H_{22}ON_2$ requires C, 83·5; H, 5·5; N, 6·9%; *M*, 402).

p-*Azoxy*-2-*nitrostilbene*. Reduction of 2 : 4-dinitrostilbene (Bishop and Brady, J., 1922, **121**, 2367) (2·6 g.) with benzoin (2·1 g.), anisoin (2·6 g.), or furoin (1·9 g.) gave 1·8 g., 1·75 g., or 1·8 g., respectively, of the p-*azoxy*-compound, which crystallised from xylene in orange plates, m. p. 208—210° (Found: C, 68·2; H, 4·2; N, 11·4; *M*, 487. $C_{28}H_{20}O_5N_4$ requires C, 68·3; H, 4·1; N, 11·3%; *M*, 492). Anisil, m. p. 133°, and furil, m. p. 162°, were obtained from their respective mother-liquors.

p-*Azoxy*-2 : 3′-*dinitrostilbene*. 2 : 4 : 3′-Trinitrostilbene (1·6 g.) and benzoin (1·1 g.) gave 0·75 g. of the reduction compound, which crystallised from xylene in yellow flakes, m. p. 212° (Found: C, 58·1; H, 3·4; N, 14·4. $C_{28}H_{18}O_9N_6$ requires C, 57·7; H, 3·1; N, 14·4%).

p-*Azoxy*-2 : 4′-*dinitrostilbene*. Only traces of this reduction compound could be isolated, since it was difficult to find a suitable solvent for the nitrostilbene.

p-*Azoxy*-2 : 6-*dinitrostilbene*. 2 : 4 : 6-Trinitrostilbene (Bishop and Brady, *loc. cit.*) (3·2 g.) and benzoin (2·1 g.) gave on standing over-night a small yield of a solid which, recrystallised from glacial acetic acid, had m. p. 270° (Found: N, 14·6. $C_{28}H_{18}O_9N_6$ requires N, 14·4%).

p-*Azoxy*-2-*nitro*-4′-*methoxystilbene*. 2 : 4-Dinitro-4′-methoxystilbene (3·1 g.) and benzoin (2·1 g.) gave 2·2 g. of the *azoxy*-compound, which is only slightly soluble in boiling xylene and is an orange-red, microcrystalline powder, m. p. 208° (Found: C, 65·8, 64·75, 64·75; H, 4·7, 4·5, 4·6; N, 10·0; *M*, 512. $C_{30}H_{24}O_7N_4$ requires C, 65·2; H, 4·3; N, 10·1%; *M*, 552).

p-*Azoxy*-2-*nitro*-3′ : 4′-*methylenedioxystilbene*. 2 : 4-Dinitro-3′ : 4′-methylenedioxystilbene (2·8 g.) and benzoin (2·1 g.) gave 1·7 g. of the p-*azoxy*-compound which, recrystallised from xylene, formed a red, microcrystalline solid, m. p. 230° (Found: C, 62·1; H, 4·0; N, 9·4; *M*, 586. $C_{30}H_{20}O_9N_4$ requires C, 62·0; H, 3·5; N, 9·6%; *M*, 580).

p-*Azoxy*-2 : 6-*dinitro*-4′-*methoxystilbene*. 2 : 4 : 6-Trinitro-4′-methoxystilbene (2·8 g.) and benzoin (2·1 g.) gave 1·25 g. of the p-*azoxy*-compound, which forms bronze plates from xylene. It changes colour at 252° and melts with decomposition at 297° (Found: C, 55·6; H, 3·6; N, 13·2. $C_{30}H_{22}O_{11}N_6$ requires C, 55·9; H, 3·4; N, 13·06%).

p-*Azoxy*-2-*nitro*-4'-*dimethylaminostilbene*. 2:4-Dinitro-4'-dimethylaminostilbene (1·5 g.) and benzoin (1 g.) gave black, flaky crystals of the p-*azoxy*-compound which were washed with hot alcohol. The compound is so slightly soluble in boiling xylene that it cannot be recrystallised from that solvent. The substance without further purification remained unchanged at 305° (Found: N, 14·3. $C_{32}H_{30}O_5N_6$ requires N, 14·5%). The compound is soluble in hot concentrated hydrochloric acid, but the hydrochloride is readily hydrolysed on addition of water. Two attempts to prepare a chloroplatinate failed owing to the almost colloidal nature of the hydrochloric acid solution.

The mother-liquors from each of the above reductions in which benzoin was used yielded benzil, m. p. 95°, on standing or when poured into water and the needles so obtained were recrystallised from alcohol. The compound was identified by its characteristic reaction with alcoholic potash and by its oxidation to benzoic acid, m. p. 122°, by means of alkaline permanganate.

The investigation is being continued with a view to establishing the generality of this method of reducing nitro- to azoxy-groups and determining its value as a method of preparing azoxy-compounds.

In concluding this part of the work, the author desires to thank Professor A. Archibald Boon for his kind interest and for providing the facilities which have rendered this research possible.

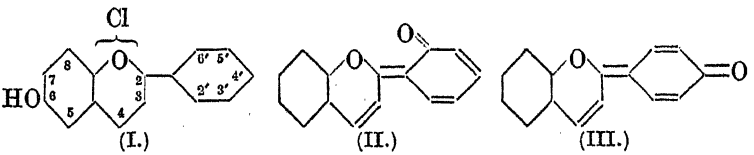
HERIOT-WATT COLLEGE, EDINBURGH. [*Received, June 20th*, 1927.]

CCLXXVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XIII. Some Monohydroxyflavylium Salts.*

By FRANK MOUATT IRVINE and ROBERT ROBINSON.

IT was thought that a study of some of the simpler hydroxyflavylium salts might throw light on the effects produced by hydroxy-groups in different positions in the three nuclei, especially from the point of view of anhydro-base and pseudo-base formation. Solutions of 3-hydroxyflavylium chloride have been obtained by demethylation of the methyl ether (Pratt and Robinson, J., 1923, **123**, 748), but this salt showed such a strong tendency to pass into the pseudo-base that it could not be isolated in a pure condition. It dissolves in sulphuric acid to a solution that exhibits intense plum-coloured fluorescence. 6-Hydroxyflavylium chloride (I) is less readily

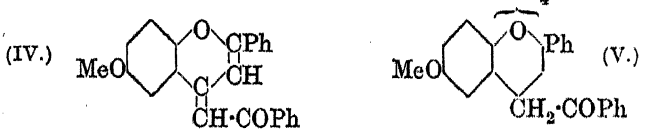
hydrolysed, but also yields a colourless pseudo-base, a quinonoid anhydro-base not being possible without the postulation of " bridge-bonds." This is merely one more example among many which



(I.) (II.) (III.)

show that aromatic structures assume a bridge-phase with the greatest reluctance. In the cases of 2′- and 4′-hydroxyflavylium salts, anhydro-bases of the types (II) and (III) are possible. Actually the anhydro-bases derived from 2′-hydroxyflavylium chloride and 2′-hydroxy-8-methoxyflavylium chloride are violet substances that could not be isolated owing to their marked tendency to pass into pseudo-bases by hydration. Thus the quinones are not formed by dehydration of pyranols, but are directly obtained from the kations of the pyrylium salts by removal of a proton under the influence of anions. The colour-base from 4′-hydroxyflavylium chloride is apparently a quinhydrone having the composition $C_{15}H_{10}O_2,C_{15}H_{12}O_3,2H_2O$; by analogy with the suggestions of Schneider and Meyer (*Ber.*, 1921, **54**, 1484) it may be named *4′-hydroxyflavanhydrone*. The molecular weight of the anhydrous compound corresponded with this formula, and similar results were obtained in the study of *4′-hydroxy-8-methoxyflavanhydrone*.

Incidentally *6-methoxy-4-phenacylideneflavene* (IV) has been examined and found to yield a *hydroferrichloride* (V) which is readily hydrolysed by water.



(IV.) (V.)

Moreover, the carbonyl group in (IV) is inactive, so that the resemblance to the pyrones is complete, the system −O−C=C−C=O being extended to −O−C=C−C=C−C=O. Probably the phenacylideneflavenes are dipoles and anhydronium bases in the sense in which that expression was used by Armit and Robinson (J., 1925, **127**, 1607). In view of the remarkable rearrangement of the anhydro-base from 2 : 6-diphenyl-4-*o*-hydroxyphenylpyrylium chloride to phenacylideneflavene (Dilthey and Floret, *Annalen*, 1924, **440**, 95), alternative formulæ for the latter substance would appear to require consideration. However, Dilthey and Floret have excluded

possibilities based on the triphenylpyrylium skeleton on the ground that phenacylideneflavene gives a small quantity of flavone when oxidised by permanganate.

EXPERIMENTAL.

8-Methoxyflavylium Chloride.—Under slightly modified conditions, the direct condensation of *o*-vanillin, acetophenone, and hydrogen chloride in acetic acid solution (Roberts and Robinson, J., 1924, **125**, 209) gave a 70% yield of the flavylium salt, which crystallised from dilute hydrochloric acid in brown needles which blackened at 170° and melted at 190° (decomp.) (Found in material dried in a vacuum: C, 66·2; H, 5·2. $C_{16}H_{13}O_2Cl,H_2O$ requires C, 66·1; H, 5·1%). The *iodide* crystallises from dilute, colourless hydriodic acid in puce-coloured needles, m. p. 134°. All attempts to demethylate these salts were unsuccessful.

Phenyl 2-Hydroxy-5-methoxystyryl Ketone.—2-Hydroxy-5-methoxybenzaldehyde (5·1 g.; 1 mol.) and acetophenone (4 g.; 1 mol.) in ethyl alcohol (30 c.c.) were mixed with a warm solution of potassium hydroxide (13 g.; 7 mols.) in water (13 c.c.) and left in a warm place over-night. The solution was poured into water (400 c.c.), kept for an hour until the waxy precipitate (A) had solidified, and then filtered. The filtrate and washings were acidified with 50% acetic acid and the chalkone was collected and dried (yield, 4·25 g. or 50%). It crystallised from benzene or from 50% alcohol in clusters of fine, golden-yellow needles, m. p. 104° (Found: C, 75·5; H, 5·4. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

The residue (A) was thrice recrystallised from alcohol; it formed stellate clumps of short, white needles, m. p. 125° (Found: C, 77·0; H, 6·0. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). The yield (2·6 g.) of this *2-hydroxy-5-methoxybenzylidenediacetophenone* was 40% of that theoretically possible. A larger percentage was formed when the temperature during the alkaline condensation was higher; but it was not found possible, by varying the molecular proportion of the alkali employed, to obtain a higher yield of the chalkone.

6-Methoxyflavylium Salts.—Phenyl 2-hydroxy-5-methoxystyryl ketone was converted into 6-methoxyflavylium chloride by means of hydrogen chloride in acetic acid solution. The reaction proceeded to completion in the cold, passing through the red ketone-hydrochloride stage. The flavylium salt partly crystallised and was partly precipitated by the addition of ether. It was collected and dried to constant weight in a vacuum (Found: C, 62·3; H, 5·5. $C_{16}H_{13}O_2Cl,2H_2O$ requires C, 62·2; H, 5·5%). The salt crystallised from 5% hydrochloric acid in dark greenish-brown, shining needles, m. p. 97°. Its yellow solution in concentrated sulphuric acid

exhibited a weak green fluorescence, but the orange-yellow alcoholic solution was non-fluorescent. The *ferrichloride* crystallised from acetic acid in glistening, brown platelets with green nuance, m. p. 203° (Found: C, 44·0; H, 3·2; Fe, 12·7. $C_{16}H_{13}O_2Cl_4Fe$ requires C, 44·1; H, 3·0; Fe, 12·9%). The *iodide* crystallised from alcohol in almost black, microscopic needles, m. p. 143°, whilst the *periodide* had m. p. 86—87°. The *perchlorate* crystallised from 60% methyl alcohol in short, dark brown needles, m. p. about 200° (decomp.).

6-*Hydroxyflavylium Salts.*—The demethylation required rather careful control. A mixture of 6-methoxyflavylium chloride dihydrate (8·8 g.), phenol (40 g.), and hydriodic acid (*d* 1·74; 150 c.c.) was heated in a glycerol-bath at 110°, until the effluent stream of carbon dioxide no longer contained methyl iodide (45 minutes). The mixture was diluted with an equal volume of water and of ether, cooled in ice, and filtered; the black crystals (6·4 g.) had a green lustre. After the ethereal layer had been separated, the remainder (about 3·6 g.) of the iodide, mixed with periodide, could be recovered by evaporating the filtrate under reduced pressure in an atmosphere of hydrogen. The demethylated product (7 g.) was dissolved in the minimum volume of hot alcohol (700 c.c.) and concentrated hydrochloric acid (200 c.c.), and freshly precipitated silver chloride (from 7 g. of silver nitrate) added. The mixture was gently boiled during 5 minutes while being stirred; it was then filtered hot, and the residue washed with hot ethyl-alcoholic hydrochloric acid. The filtrate and washings were concentrated to a small volume and cooled, and the 6-*hydroxyflavylium chloride* was collected; it crystallised from alcohol or from 15% hydrochloric acid in orange needles. The chloride was very readily hydrolysed by water, and the pseudo-base was also formed when sodium acetate was added. The *ferrichloride* crystallised from glacial acetic acid in short, reddish-brown needles, m. p. 198° (Found: C, 43·1; H, 2·7; Fe, 13·2. $C_{15}H_{11}O_2Cl_4Fe$ requires C, 42·8; H, 2·6; Fe, 13·3%). The *chloroaurate* formed golden-brown needles which on heating turned grey at 180° but did not melt. 6-Hydroxyflavylium salts give, in concentrated sulphuric acid, orange solutions with a green fluorescence.

4′-*Hydroxyflavylium Salts.*—*p*-Methoxyacetophenone was condensed with salicylaldehyde to form *p*-methoxyphenyl *o*-hydroxystyryl ketone as described by Kostanecki and Zwayer (*Ber.*, 1908, **41**, 1337) and the yield of the pure, recrystallised product was 81%. The chalkone (13·8 g.) was dissolved in a mixture of glacial acetic acid (50 c.c.) and concentrated hydrochloric acid (25 c.c.) by saturating this with hydrogen chloride, and the solution after an hour was gently warmed for 15 minutes and poured into water. An

excess of potassium iodide was added to the filtered solution of the flavylium chloride and an orange precipitate of the anhydrous *4'-methoxyflavylium iodide* was formed (yield, 89%). This salt (17·2 g.) was gently refluxed for ½ hour with hydriodic acid (300 c.c.; *d* 1·74) and phenol (70 g.) in an atmosphere of carbon dioxide. On cooling, crystals (9·4 g.) separated which were pure enough for the next operation; for analysis, they were recrystallised from methyl alcohol, being thus obtained in dark purple prisms (Found: C, 29·8; H, 2·0; I, 62·7. $C_{15}H_{11}O_2I_3$ requires C, 29·8; H, 1·8; I, 63·1%). *4'-Hydroxyflavylium periodide* melts at 208—209° and decomposes suddenly at 285°; when pressed on glass, it has a beetle-green lustre. Freshly precipitated silver chloride (from 2·85 g. of silver nitrate) was added to a solution of the periodide (2 g.) in a hot mixture of methyl alcohol (125 c.c.) and 7·5% hydrochloric acid (100 c.c.), and the whole was boiled for 15 minutes and filtered. The filtrate and washings were concentrated and, on cooling, red needles separated (yield, 80%). This product was crystallised several times from dilute hydrochloric acid in order to remove traces of inorganic impurities which were tenaciously held. The clusters of fine, orange-red needles, after drying over sulphuric acid and potassium hydroxide, darkened at 135° and melted at 142° (decomp.) (Found: C, 61·2, 61·0; H, 5·1, 5·3. $C_{15}H_{11}O_2Cl,2H_2O$ requires C, 61·1; H, 5·1%). This salt dissolves in water or alcohol to an orange solution which becomes yellow on the addition of a drop of dilute hydrochloric acid or red with weakly alkaline reagents. The orange solution in concentrated sulphuric acid exhibits a green fluorescence. The *chloroaurate* crystallises in golden-orange needles, m. p. 177°.

4'-Hydroxyflavanhydrone.—A solution of 4'-hydroxyflavylium chloride in water was covered with benzene, and excess of sodium acetate added; on shaking, a portion of the violet-red substance was dissolved by the benzene, which was separated, dried with potassium carbonate, and filtered. The dark violet solid which remained on removal of the solvent could not be crystallised (Found: C, 72·0; H, 5·7; loss on heating at 110°/15 mm., 7·4. $C_{30}H_{22}O_5,2H_2O$ requires C, 72·3; H, 5·2; H_2O, 7·2%. Found in dried material: C, 77·6; H, 4·9; *M*, by micro-Rast, 472. $C_{30}H_{22}O_5$ requires C, 77·9; H, 4·8%; *M*, 462). On further heating, the deep red substance gradually sintered and was completely molten at 200°. The red solution in pyridine became colourless in a few seconds, probably as the result of the formation of the benzopyran ether (compare Dilthey, *J. pr. Chem.*, 1917, **95**, 113, 117). This flavanhydrone showed no tendency to combine with methyl iodide.

4'-Hydroxy-8-methoxyflavylium Salts.—The method of Nencki and

Stoeber (*Ber.*, 1897, **30**, 1769) for the preparation of *p*-hydroxyacetophenone only gives a 10% yield and the product is difficult to purify. The following modification is much more satisfactory: Powdered anhydrous ferric chloride (81 g.) was added to a solution of phenol (63 g.) in carbon disulphide (48 c.c.), and acetyl chloride (95 c.c.) was then introduced drop by drop with shaking. When the addition was complete, the mixture was shaken during 5 minutes and the carbon disulphide and acetyl chloride were then carefully removed by distillation. The residue was decomposed by water and rendered alkaline with sodium hydroxide, the solution decanted from the ferric hydroxide, which was washed by decantation, and the crude *p*-hydroxyacetophenone precipitated by acidification. After crystallisation from water, 30 g. (yield, 33%), m. p. 110°, were obtained. p-*Acetoxyacetophenone*, m. p. 54°, crystallises from alcohol and was obtained in 80% yield on agitating an aqueous solution of sodium *p*-acetylphenoxide (1 mol.) with acetic anhydride (1 mol.).

A stream of hydrogen chloride was passed through a solution of *o*-vanillin (1·1 g.) and *p*-hydroxyacetophenone (1 g.) in formic acid (10 c.c.) for 1 hour, and the mixture kept until next day. The orange solid precipitated on the addition of ether crystallised from 10% hydrochloric acid (60 c.c.) in brick-red needles (1·6 g.) (Found in material dried in a vacuum: C, 62·3; H, 4·8. $C_{16}H_{13}O_5Cl,H_2O$ requires C, 62·6; H, 4·9%). This salt darkens at 170° and melts at 190° (decomp.); it dissolves in water to a yellow solution exhibiting a weak green fluorescence. The *ferrichloride* crystallised from acetic acid in reddish-brown needles, m. p. 217°, and the *periodide* crystallised in chocolate-coloured needles, m. p. 170—173° (decomp.), after darkening at 140°. The ruby benzene solution of the anhydro-base, prepared in the usual manner, was dried with potassium carbonate and, on removal of the solvent from the filtered solution, a deep purplish-red solid residue was obtained, which was dried in a vacuum (Found: C, 73·7; H, 5·4. $C_{32}H_{26}O_7$ requires C, 73·6; H, 5·0%). The molecular weight could not be determined by Rast's method and no solvent was found to be suitable for recrystallisation; in several solvents, for example, acetone and nitrobenzene, it gave bottle-green solutions. On heating, this 4′-*hydroxy*-8-*methoxyflavanhydrone* gradually sintered and decomposed at 206°.

2′-*Hydroxyflavylium Ferrichloride*.—The condensation of salicylaldehyde with *o*-hydroxyacetophenone (Fries and Pfaffendorf, *Ber.*, 1910, **43**, 215), under conditions similar to those mentioned below, gave a bright scarlet, very sparingly soluble solid, which is not a flavylium salt and is apparently of complex constitution.

The hydroxyl group in the ketonic component was therefore protected by acetylation (compare Friedländer and Neudorfer, *Ber.*, 1897, **30**, 1080; Lesser and Gad, *Ber.*, 1926, **59**, 233). A solution of *o*-acetoxyacetophenone (0·9 g.) and salicylaldehyde (0·6 g.) in formic acid (6 c.c.) was saturated with hydrogen chloride during 3 hours, and next day the red solid, which was precipitated on the addition of ether, was collected and extracted with 17% hydrochloric acid (60 c.c.), leaving a considerable residue. A *ferrichloride* prepared from the filtered solution crystallised from acetic acid in tufts of brown needles, m. p. 125° (Found: C, 42·6; H, 2·7; Fe, 13·3. $C_{15}H_{11}O_2Cl_4Fe$ requires C, 42·8; H, 2·6; Fe, 13·3%). The orange solution in sulphuric acid exhibits a weak green fluorescence. The solution of the ferrichloride in dilute hydrochloric acid gave, with a large excess of sodium carbonate solution, quickly added, a transient purple colour. The colourless filtrate from the ferric hydroxide apparently contained pseudo-base in solution, for on acidification it turned bright yellow, and then, on addition of a large excess of sodium carbonate, the purple colour flashed out, but the solution became almost instantaneously colourless. The purple colour was formed only if the sodium carbonate was added quickly and in large excess.

2′-*Hydroxy*-8-*methoxyflavylium Salts*.—Several attempts to prepare 2′-hydroxy-8-methoxyflavylium chloride by condensing *o*-vanillin (1 mol.) and *o*-acetoxyacetophenone (1 mol.) in anhydrous formic acid with hydrogen chloride failed during the recrystallisation from hot dilute hydrochloric acid (in order to remove the acetyl group in the 2′-position), probably because some complex substance, not a pyrylium salt, was formed in this case also. The use of unacetylated *o*-hydroxyacetophenone led to better results in this instance. A solution of *o*-hydroxyacetophenone (1·4 g.) and *o*-vanillin (1·5 g.) in formic acid (6 c.c.) was saturated with hydrogen chloride for 1·5 hours and on the following day ether precipitated a reddish-brown solid, which crystallised from methyl alcohol in long, red needles; these darkened above 100° and had m. p. 188° (decomp.) (Found: C, 66·3; H, 4·7. $C_{16}H_{13}O_5Cl$ requires C, 66·5; H, 4·5%). This salt dissolved in sulphuric acid to an orange solution exhibiting a weak green fluorescence. When water was added to the solid chloride or to its solution in alcohol, the pseudo-base was obtained; this dissolved with difficulty in dilute hydrochloric acid. Sodium acetate, added in excess to an acid solution of this salt, produced the violet colour-base, which could be extracted by benzene; the colour of the violet solution, however, soon faded. Again, when the colour-base was quickly separated, the filtrate was always found to contain pseudo-base. This remarkable ease of

hydration of the anhydro-base derived from a flavenol has not previously been observed in the absence of a substituent in position 3.

6-*Methoxyphenacylideneflavene* (V).—Following the details given by Feuerstein and Kostanecki (*Ber.*, 1898, **31**, 710) in the case of the parent substance, 2-hydroxy-5-methoxybenzylidenediacetophenone (7·5 g.) was converted into acetophenone (1·1 g.), *phenyl* β-2-*hydroxy*-5-*methoxyphenylethyl ketone* (2·3 g.), and 6-*methoxyphenacylideneflavene* (3·8 g.). The last compound crystallised from alcohol or benzene in yellow, feathery clusters of fine needles, m. p. 146° (Found: C, 80·7, 80·8; H, 5·0, 5·0; MeO, 8·8. $C_{24}H_{18}O_3$ requires C, 81·4; H, 5·1; MeO, 8·8%). In the micro-Zeisel determination, the mixture required to be heated almost twice as long as usual. The solution in cold sulphuric acid was yellowish-orange and non-fluorescent, and on warming a transitory purple colour appeared, succeeded by a ruby one.

Pure 6-methoxyphenacylideneflavene (1·8 g.) was suspended in acetic acid (10 c.c.), and a stream of dry hydrogen chloride passed during 3 minutes; on shaking, all the solid dissolved to a red solution. The addition of a solution of anhydrous ferric chloride (0·8 g.) in glacial acetic acid (5 c.c.) produced an immediate red precipitate, which soon became brownish-orange and crystalline. After keeping for an hour, the flask being stoppered, the solid was collected and dried over sulphuric acid and potassium hydroxide (yield, 2·54 g. or 92%) (Found: C, 52·0; H, 3·5; Fe, 10·0; MeO, 5·8. $C_{24}H_{19}O_3Cl_4Fe$ requires C, 52·1; H, 3·4; Fe, 10·1; MeO, 5·6%).

6-*Methoxy*-4-*phenacylflavylium ferrichloride* forms microscopic, elongated prisms which melt, with blackening, at 170° (on slow heating). It is sparingly soluble in water to an orange solution which slowly deposits 6-methoxyphenacylideneflavene; this hydrolysis is, however, very rapid in presence of alcohol. The ferrichloride gives an orange, non-fluorescent solution in sulphuric acid.

6-Methoxyphenacylideneflavene (1 mol.) did not react when refluxed in benzene solution for ½ hour with magnesium phenyl bromide (1 mol. prepared in ether).

The *phenyl* β-2-*hydroxy*-5-*methoxyphenylethyl ketone* was a brown syrup with a strong green reflex. Although its hydroxyl group could not be acetylated or benzoylated, its carbonyl group was reactive, and the *semicarbazone* and p-*nitrophenylhydrazone* were readily prepared. The former crystallised from alcohol in white, elongated prisms, m. p. 184° (Found: C, 65·1; H, 6·5; N, 13·5. $C_{17}H_{19}O_3N_3$ requires C, 65·2; H, 6·1; N, 13·4%), and the latter separated from alcohol in microscopic, orange needles, m. p. 163—

165°. The ketone itself could not be crystallised. The same hydrochalkone was obtained, also as a syrup, and identified as the semicarbazone, m. p. 184° (alone or mixed), by the catalytic reduction of phenyl 2-hydroxy-5-methoxystyryl ketone with a palladium catalyst.

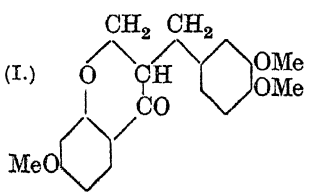
THE UNIVERSITY, MANCHESTER. [*Received, June 28th*, 1927.]

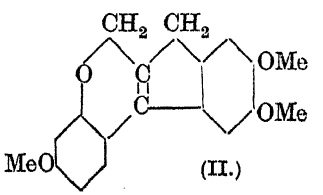
CCLXXVII.—*Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part II. A Synthesis of Deoxytrimethylbrazilone and of* iso*Brazilein Ferrichloride Trimethyl Ether.*

By WILLIAM HENRY PERKIN, jun., JNANENDRA NATH RÂY, and ROBERT ROBINSON.

IN Part I of this investigation (J., 1926, 941) it was explained that our object in attempting the preparation of 3-homoveratryl-7-methoxychromanone (I) was to examine its behaviour towards dehydrating agents, which should convert it into the indene derivative (II), a near relative of *O*-trimethylbrazilin.

(I.)



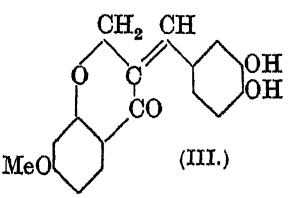


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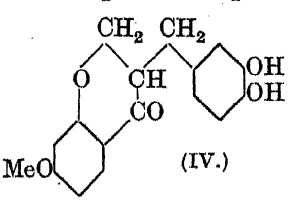
Considerable progress in this direction has since been made and we had hoped to be able to defer publication until our experiments on the final stages of the synthesis of trimethylbrazilin were completed; an interim report has, however, become necessary as the result of a communication received on June 7th from Professor P. Pfeiffer and we therefore submit at once an account of the stage already reached in our work. Professor Pfeiffer's letter mentions results similar in many respects to those which we have obtained and in view of this duplication of research we wish to direct attention to the clear statement of our position which we thought it wise to make at the time of publication of Part I of this series (*loc. cit.*, p. 942) and which it is unnecessary to repeat. The reduction of veratrylidene-7-methoxychromanone by means of hydrogen in presence of palladium yielded (*loc. cit.*, p. 946) 3-homoveratryl-7-methoxychroman, m. p. 96°, instead of the expected ketone (I), which, however, Pfeiffer and Emmer (*Ber.*, 1920, **53**, 945) claimed

to have obtained when they employed platinum as the catalyst. The ketone was stated to melt at 89° and in Part I we expressed some doubt in regard to the accuracy of the interpretation of their results. Since, however, we had not repeated these experiments, our remarks were guarded and summarised in the statement (p. 947): "We do not go so far as to assert that the products of hydrogenation of veratrylidenemethoxychromanone in presence of platinum and of palladium are identical, although we think it probable that this will prove to be the case." The suggestion so expressed was, however, not correct, as the experiments mentioned below indicate, and Professor Pfeiffer informs us that he has re-examined his substance and proved that it is a ketone by the preparation of its oxime. Although we were unable to accomplish satisfactorily the reduction of veratrylidenemethoxychromanone to a related saturated ketone, the formation of the saturated ketone (IV) from 3 : 4-dihydroxybenzylidene-7-methoxychromanone (III) proceeds smoothly under these conditions.

This substance (III) was obtained by the condensation of protocatechualdehyde with 7-methoxychromanone (a new and improved method for the preparation of which is described on p. 2097) in acetic acid solution by means of hydrogen chloride. On methylation in the usual manner, (IV) yields the ketone (I), which has m. p. 92°, and the whole of the substance which we have used in this investigation was prepared in this way. Subsequently the same compound was isolated in poor yield from the products of the partial hydrogenation of veratrylidenemethoxychromanone in presence of palladium.



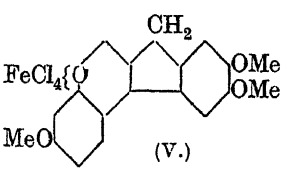
(III.)



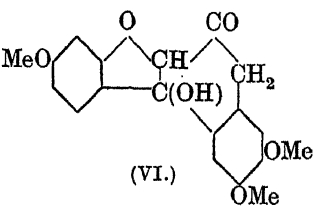
(IV.)

On treatment with phosphoric anhydride in boiling benzene the dehydration of (I) to (II) was effected, and the first indication of its structure and of the fact that it contains the brazilin skeleton was provided by the oxidation of the crude substance to *iso*brazilein ferrichloride trimethyl ether (V) (Engels, Perkin, and Robinson, J., 1908, **93**, 1121; Crabtree and Robinson, J., 1918, **113**, 859), a process effected by means of ferric chloride in acetic acid solution. The salt was identified by comparison with an authentic specimen prepared from brazilein. Later, the compound (II) was obtained from (I) in a pure condition by the dehydrating action of phosphoric anhydride and identified by direct comparison with deoxytrimethyl-

brazilone, $C_{19}H_{18}O_4$, a substance obtained by the reduction of trimethylbrazilone, $C_{19}H_{18}O_6$, with phenylhydrazine (Gilbody and Perkin, J., 1902, **81**, 1046). Deoxytrimethylbrazilone, prepared from brazilin, was also found to yield the *iso*brazilein derivative in the manner described above. Professor Pfeiffer's letter directs attention to the possibility that his dehydration product of the ketone (I) may be deoxytrimethylbrazilone and that the pyrylium salt which it yields on oxidation with ferric chloride may be *iso*-brazilein ferrichloride trimethyl ether. The synthetical proof that deoxytrimethylbrazilone has the constitution (II) and contains the brazilin skeleton necessitates a view of the nature of trimethylbrazilone differing somewhat from that expressed in the formula (VI) (Perkin and Robinson, J., 1908, **93**, 948). It was then suggested that the oxidation of trimethylbrazilin with chromic acid leads to the disruption of the bond common to the chroman and hydrindene nuclei and to the production of a diketone (VII) which passes into (VI) by an intramolecular aldol condensation. In harmony with the conclusions drawn by Professor J. F. Thorpe and his collaborators from extensive researches on ring-chain and intra-annular tautomerism (VI) and (VII) might be regarded as tautomerides.

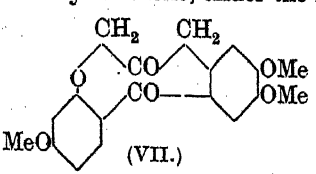


(V.)

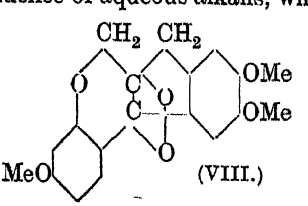


(VI.)

Bearing in mind the phenomena encountered by Willstätter in his study of the *o*-quinones and by Schönberg among the benzils (compare *Annual Reports*, 1922, 109), we might also postulate the peroxidic phase (VIII), the complete tautomeric system being (VI) $\rightleftharpoons$ (VII) $\rightleftharpoons$ (VIII). The phase (VI) must be, at least, an intermediate in the formation of the β-naphthol derivative, α-anhydrotrimethylbrazilone, under the influence of aqueous alkalis, whilst



(VII.)



(VIII.)

VIII) offers an explanation of the remarkable behaviour with phenylhydrazine. Nevertheless, (VI) and (VIII) can only be

related through (VII) and the last seems to be the most satisfactory single expression of the whole character of trimethylbrazilone which it is possible to select. In this phase, some coherence of the carbonyl groups may be manifested as the result of the dipolar character of these groups.

Further evidence bearing on this aspect of the chemistry of brazilin will, it is hoped, be discussed in a future communication and it is proposed to extend the synthetical work indicated above to the analogous hæmatoxylin derivatives. Naturally we are also engaged in attempts to convert deoxytrimethylbrazilone into trimethylbrazilin.

EXPERIMENTAL.

7-Methoxychromanone.—The following method of preparation of this substance is much more convenient than any of those hitherto described. A solution of β-*m*-methoxyphenoxypropionic acid (14 g.) in 80% sulphuric acid (100 c.c.) was heated to 60° during an hour, then at 60—80° for an hour, and finally at 80—90° for a third hour. The ketone was isolated by means of ether in the usual manner from the diluted mixture and freed from acids. The crude product crystallised when dry and weighed 7—8 g. (yield, about 60%). Several new substances which have been prepared in the course of our work may be mentioned here. *Ethyl* β-m-*methoxyphenoxypropionate,* $MeO\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot CO_2Et$, obtained by esterification of the acid with boiling ethyl-alcoholic sulphuric acid, crystallises from aqueous alcohol in plates, m. p. 45° (Found: C, 63·8; H, 7·3. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%). This ester could not be condensed with veratraldehyde. *Veratrylidene-7-methoxychromanone dibromide,* prepared in cold carbon tetrachloride solution, has m. p. 137—138° (Found: C, 46·2; H, 3·6. $C_{19}H_{18}O_5Br_2$ requires C, 46·8; H, 3·7%) and yields veratrylidenemethoxychromanone on treatment with zinc dust and acetic acid.

Veratrylidenemethoxychromanone yields an *oxamino-oxime* when treated with hydroxylamine hydrochloride (3 mols.) and sodium acetate in boiling alcoholic solution. The colourless substance crystallises from alcohol in prismatic needles (Found: C, 61·0; H, 5·8; N, 7·0. $C_{19}H_{22}O_6N_2$ requires C, 61·0; H, 5·9; N, 7·5%).

3-(3′ : 4′-Dihydroxybenzylidene)-7-methoxychromanone (III).—An ice-cold solution of 7-methoxychromanone (5 g.) and protocatechualdehyde (5 g.) in acetic acid (30 c.c.) was saturated with hydrogen chloride and set aside. Next day, the garnet crystals which had separated were collected and decomposed by trituration with water at 0°. The substance crystallised from aqueous alcohol (charcoal) in brownish-yellow, microscopic needles, m. p. 212° (Found: C, 68·5; H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%).

The alcoholic solution develops a green coloration on the addition of ferric chloride. Aqueous alkaline solutions are deep crimson to blood-red according to the concentration. Methylation by means of methyl sulphate and sodium hydroxide yields veratrylidene-methoxychromanone, m. p. 141°.

3-(3′ : 4′-*Dihydroxybenzyl*)-7-*methoxychromanone* (IV).—A solution of dihydroxybenzylidenemethoxychromanone (1·5 g.) in alcohol (100 c.c.) to which palladous chloride (15 c.c. of 0·5% aqueous solution) had been added was stirred with hydrogen; 60 c.c. of the gas were absorbed at 15° in 28 minutes. The nearly colourless liquid was filtered and concentrated; the reduction product, then precipitated on dilution with water, crystallised from aqueous alcohol (about 20%) in rectangular plates, m. p. 138° (Found: C, 68·0; H, 5·7. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). Ferric chloride added to an alcoholic solution of this substance produces a green coloration changing to crimson on keeping. The cherry-red solution in sulphuric acid soon acquires a yellowish-green fluorescence and on addition of water a fluorescent orange solution is obtained. The action of hydrogen chloride on this ketone in glacial acetic acid solution yielded, together with other products, a crystalline *substance*, m. p. 139° (mixed, 118—124°), the investigation of which is not yet complete.

3-*Homoveratryl*-7-*methoxychromanone* (I).—(A) The dihydric phenol described in the last section was methylated in methyl-alcoholic solution by means of methyl sulphate and potassium hydroxide in the usual manner; the product crystallised from aqueous alcohol and then from aqueous acetone in glistening, rectangular plates, m. p. 92° (Found: C, 70·1; H, 6·3. Calc. for $C_{19}H_{20}O_5$: C, 69·6; H, 6·1%). The substance is insoluble in aqueous alkalis and gives no coloration with ferric chloride in alcoholic solution.

(B) When veratrylidenemethoxychromanone was reduced in acetic acid solution by means of the calculated volume of hydrogen in presence of palladium the greater part of the unsaturated ketone was recovered unchanged, whilst an unlimited reduction gave homoveratrylmethoxychroman, m. p. 96°, as previously described (*loc. cit.*). Under the following conditions, however, the dihydro-derivative could be isolated, although in poor yield. A solution of veratrylidenemethoxychromanone (1·4 g.) in pure acetic acid (100 c.c.) to which palladous chloride (20 c.c. of 0·5% solution) had been added was agitated with hydrogen at 18°; 50 c.c. were absorbed in 12 minutes, and a further 50 c.c. in 50 minutes, after which absorption of a third equal volume occurred at 40—45°. The filtered solution was concentrated under diminished pressure

to 35 c.c., and water (10 c.c.) added, causing the precipitation of unchanged material, which was crystallised from alcohol (0·7 g., m. p. 141°). The acetic acid and alcoholic filtrates were diluted with water and the precipitated material was fractionally crystallised from aqueous alcohol and aqueous acetone. About 0·1 g. of a substance crystallising in glistening, rectangular plates, m. p. 92°, was isolated. The m. p. of a mixture with the ketone prepared as described under (A) was 92°, whilst a mixture with homoveratrylmethoxychroman, m. p. 96°, melted at 71—86°. A minute amount of the chroman derivative, m. p. 96°, was isolated from the mother-liquors.

Deoxytrimethylbrazilone (II).—There are indications that 3-homoveratrylmethoxychromanone may be dehydrated by means of a variety of condensing agents, *e.g.*, zinc chloride, stannic chloride, phosphoryl chloride, etc., in that the products are partly oxidised in acid solution to *iso*brazilein salts, the fluorescence of which is so characteristic. Phosphoric anhydride (30 g.) was added to a solution of the ketone (3·5 g.) in benzene (150 c.c.), and the solution gently boiled for 10 minutes. The dark mass was decomposed by the addition of ice, the mixture was heated and agitated, the benzene layer, separated from the strongly fluorescent aqueous solution, was washed with water and aqueous sodium hydroxide, dried with potassium carbonate (charcoal), and filtered, and the solvent was removed in a vacuum. The residue (R) was dissolved in alcohol, and the solution concentrated; the substance which separated on keeping crystallised from alcohol as a satiny mass of colourless sheaves of needles, m. p. 166—171°. This substance was found by direct comparison to be identical with deoxytrimethylbrazilone prepared by the method of Gilbody and Perkin (*loc. cit.*). This and also a mixture of the two specimens had m. p. 166—171°. The colour reactions and solubilities described by Gilbody and Perkin were identical in the cases of the synthetical specimen and that derived from brazilin. Some more details regarding the characteristic reactions of this substance may be given. The solution in an excess of nitric acid is intense eosin-red rather than purple (Gilbody and Perkin) and on dilution with water gives a clear red solution exhibiting very bright yellowish-green fluorescence. The more blue-toned red solution results, however, if the volume of nitric acid employed is greatly diminished, and dilution with water then gives the purple precipitate mentioned by Gilbody and Perkin. A benzene solution was treated with dilute nitric acid (1 vol., *d* 1·42, and 2 vols. of water); a crimson colour then appeared in both layers accompanied by intense yellowish-green fluorescence. On shaking, an orange substance separated from the benzene layer, the colour of which

faded. An acetic acid solution treated with a trace of bromine becomes intense crimson and the usual fluorescence is almost absent; on boiling, the colour changes to orange and dark green fluorescence appears. This becomes brilliant on dilution with alcohol and is of the *iso*brazilein type. Iodine, in most solvents, gives a similar reaction. Bromine, in an acetone solution containing hydrobromic acid, however, immediately oxidises the chromene to the pyrylium bromide, which separates in orange needles. The substance was recognised by conversion into the ferrichloride, identical with the product obtained by the method given below.

iso*Brazilein Ferrichloride Trimethyl Ether* (V).—A characteristic property of deoxytrimethylbrazilone is the ease with which it is oxidised in acid solution with formation of the *iso*brazilein salts and a convenient method is provided by the use of ferric chloride in acetic acid solution. The deoxytrimethylbrazilone was dissolved in warm acetic acid, the solution cooled, and anhydrous ferric chloride introduced; the ferrichloride soon separated as a crimson mass of needles that appeared orange by transmitted light. In some cases, and especially if cooling was used, a deep crimson ferrichloride separated in slender needles and the solution remained red. This was an intermediate product and, on gently warming, the solution became orange and the brownish-orange *iso*brazilein ferrichloride trimethyl ether separated at once. In this form the substance was practically pure and after one crystallisation from acetic acid was identified by careful comparison with a specimen obtained from pure tetramethyldihydrobrazileinol (Engels, Perkin, and Robinson, *loc. cit.*). At a much earlier stage of the investigation, the residue (R) mentioned in the last section was submitted to similar treatment; the ferrichloride so obtained crystallised from glacial acetic acid in slender, orange needles and was directly compared with an exceptionally pure specimen of *iso*brazilein ferrichloride trimethyl ether, with the result that no differences could be detected. The comparison was made in almost the same manner as that instituted by Crabtree and Robinson (*loc. cit.*) with a similar purpose in view and in all cases the properties of the specimens were examined side by side. It is not considered necessary to reproduce the account of these properties, since important variations from the description were not observed.

THE UNIVERSITIES OF OXFORD AND MANCHESTER.

[*Received, June 27th*, 1927.]

CCLXXVIII.—*Esterification in Mixed Solvents.*

By BALWANT WASUDEO BHIDE and HERBERT EDMESTON WATSON.

PREVIOUS experiments (Bhide and Sudborough, *J. Indian Inst. Sci.*, 1925, **8A**, 89) have shown that the equation $(r - a) \log a/(a - x) - x = kt$ suggested by Goldschmidt and Udby (*Z. physikal. Chem.*, 1907, **60**, 728) gives satisfactory values for the velocity coefficient k in numerous cases of esterification of organic acids with ethyl alcohol, and thus allows for the effect of the water formed during the reaction. The question as to the actual catalytic agent is, however, still obscure. Of the theories which have been put forward (compare Lapworth, J., 1911, **99**, 1427; Rice *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 2808; 1924, **46**, 2405; 1925, **47**, 379), that of Goldschmidt (*Z. physikal. Chem.*, 1913, **81**, 30; 1920, **94**, 233), according to which both the hydrogen ions and the undissociated molecules are assumed to act as catalysts, has given satisfactory results in explaining the enolisation of acetone, the decomposition of diazoacetates, and the esterification of certain acids with methyl and ethyl alcohols, for a range in concentration of the catalyst from 0·05 to 0·2*N*. As the degree of dissociation between these limits only changes by approximately 10%, the relative effects of the ions and molecules cannot be determined with great accuracy.

In order to study the question through a greater range of ionic concentration, it was decided to examine the effects obtained in the presence of non-dissociating solvents. Kailan (*Z. physikal. Chem.*, 1914, **88**, 63) has shown that the velocity coefficient for the esterification of benzoic acid by ethyl alcohol is largely increased when benzene is added, but he has not worked with solutions containing more than 75% of benzene.

In the present experiments, mixtures of *iso*amyl alcohol with benzene or ligroin have been used. As acids, suberic and *n*-butyric were selected on account of their convenient rates of esterification. The former is moderately easily soluble in *iso*amyl alcohol (5·15 g. per 100 g. of solvent), but almost insoluble in benzene and ligroin. The latter is miscible in all proportions with all three solvents.

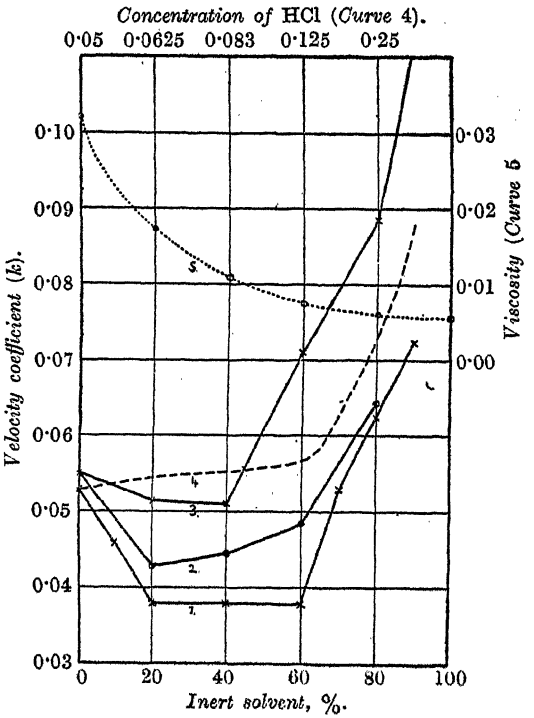
EXPERIMENTAL.

The *iso*amyl alcohol was very carefully purified and dried, the final drying agent being anhydrous copper sulphate, as metallic calcium was found to give rise to traces of ammonia which increased the conductivity. At 30°, it had d 0·8026 and specific conductivity 2×10^{-7} mho. The suberic acid had m. p. 140°; *n*-butyric

acid, b. p. 156—157°/685 mm.; and benzene, $d_4^{30°}$ 0·8658. The ligroin dried over sodium had b. p. 80—90°/685 mm., and did not decolorise bromine. Throughout the preparation and subsequent use of these materials, the utmost care was taken to exclude moisture.

The composition of mixtures is given as % by vol., and density determinations showed that the change of volume on mixing was negligible.

FIG. 1.



Curve 1. *Suberic acid–benzene.* 2. n-*Butyric acid–benzene.* 3. n-*Butyric acid–ligroin.* 4. *Suberic acid–*iso*amyl alcohol with varying* HCl. 5. *Viscosity:* iso*amyl alcohol–benzene.*

Several determinations of the viscosity and conductivity of the solutions were made in order to ascertain whether these properties could be correlated with the velocity coefficients.

Viscosity measurements were made with an Ostwald viscometer at 30° ± 0·05° and the results are in Table I and Fig. 1 (Curve 5).

When hydrogen chloride is dissolved in *iso*amyl alcohol, the viscosity increases regularly with the concentration, rising from 0·0321 for the pure alcohol to 0·0354 for a 0·142*N*-solution.

TABLE I.

Viscosity of mixtures of *iso*amyl alcohol and benzene.

Benzene, %.	Time of flow (secs.).	$d_4^{20°}$.	η.	Benzene, %.	Time of flow (secs.).	d_4^{30}.	η.
0	419·0	0·8026	0·0321	60	95·0	0·8397	0·00760
20	222·4	0·8147	0·0173	80	76·4	0·8525	0·00621
40	137·4	0·8266	0·0108	100	68·0	0·8658	0·00562

Conductivity measurements of solutions of hydrogen chloride in the anhydrous solvents were made, but were rendered difficult by the large decrease in conductivity caused by traces of water. Table II shows the effect of water upon the equivalent conductivity (Λ) of a 0·1*N*-solution of hydrogen chloride in *iso*amyl alcohol;

TABLE II.

Conductivity of 0·1*N*-*iso*amyl alcohol solutions of HCl containing water.

H_2O (mols./litre)	0·0	0·078	0·163	0·203	0·248	0·31	0·62	1·05
Λ	2·18	1·62	1·494	1·491	1·490	1·64	1·99	2·33

it will be observed that the conductivity drops rapidly to a minimum and then steadily rises. Analogous results have been obtained by Goldschmidt (*Z. physikal. Chem.*, 1915, **89**, 129) in the case of ethyl alcohol. Consistent results could only be obtained by making a fresh solution in the conductivity cell itself for each determination.

Table III gives the results obtained for *iso*amyl alcohol alone and for 20 and 40% benzene solutions.

TABLE III.

Conductivity of HCl in *iso*amyl alcohol.

HCl (*N*)	0·00565	0·0166	0·0216	0·0303	0·055	0·071	0·086	0·110	0·164
Λ	2·42	2·33	2·28	2·21	2·18	2·16	2·15	2·20	2·27

Conductivity of HCl in *iso*amyl alcohol containing 20% of benzene.

HCl (*N*)	0·0133	0·0250	0·0385	0·0425	0·0675	0·0773
Λ	1·040	0·917	0·883	0·886	0·923	0·958

Conductivity of HCl in *iso*amyl alcohol containing 40% of benzene.

HCl (*N*)	0·0171	0·0196	0·0308	0·0443	0·074	0·103	0·132
100Λ	1·43	1·36	1·27	1·33	1·53	1·83	2·22

In all these solutions Λ has a minimum value. Godlewski (*J. Chim. physique*, 1905, **3**, 432) has observed a similar minimum for the case of acetic acid in amyl alcohol.

The conductivities of solutions with a higher proportion of benzene were very low, *e.g.*, 0·088*N*-hydrogen chloride in 60% benzene solution had an equivalent conductivity of $7·1 \times 10^{-4}$ mho.

Reaction Velocity.

The rate of esterification was measured in the manner previously described (Bhide and Sudborough, *loc. cit.*) at 30° ± 0·01°. At this temperature the concentration of a 0·05*N*-solution of hydrogen chloride in *iso*amyl alcohol remained unchanged for more than 48 hours. As the reaction with suberic acid was practically complete in 7 hours, no complication was produced by reaction between the alcohol and hydrogen chloride.

According to Goldschmidt the value of r in his formula is constant for any one alcohol. It may be calculated by taking a series of readings during the course of an esterification and solving for k and r from two of the simultaneous equations so obtained. In the present case, r was determined from esterification experiments with both suberic and acetic acids, and the mean value 0·11 was found to yield values of k which were in good agreement with each other in every experiment, so that it is not necessary to give detailed results. The final values for the velocity coefficients are in all cases the mean of at least two concordant determinations.

Preliminary experiments showed that the velocity coefficient was not proportional to the concentration of catalyst but became relatively greater as the concentration increased. In all subsequent experiments the concentration of hydrogen chloride was kept as near to 0·05*N* as possible.

Table IV shows the extent of this variation for the esterification of 0·1*N*-suberic acid by *iso*amyl alcohol. The coefficients given are calculated for 0·05*N* catalyst on the assumption that the velocity coefficient is proportional to the concentration of catalyst.

TABLE IV.

Change in velocity coefficient with catalyst concentration.

HCl (*N*)	0·0045	0·012	0·050	0·100	0·220	0·464
k for 0·05*N*-HCl	0·036	0·045	0·053	0·056	0·071	0·086

Goldschmidt and Udby's formula was found not to give a constant for the highest concentration of acid, the value of k increasing with time. The figure 0·086 in the table is the initial value.

Table V shows the velocity coefficients for 0·1*N*-suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol and benzene with 0·05*N*-hydrogen chloride as catalyst.

As has been pointed out by Kailan (*loc. cit.*), the quantity k, although constant in any one experiment, is not proportional to the true velocity coefficient when the composition of the solvent is altered. The general equation for a second-order reaction may be written $dx/dt = k_1Cc$, where C and c are the concentrations of

TABLE V.

Velocity coefficients of 0·1*N*-suberic and *n*-butyric acids.

	Suberic acid.		*n*-Butyric acid.	
Benzene, %.	$k \times 10^4$.	$k_1 \times 10^4$.	$k \times 10^4$.	$k_1 \times 10^4$.
0	535	535	550	550
10	458	509		
20	380	475	430	537
40	381	635	446	743
60	378	945	487	1220
70	531	1770		
80	625	3130	645	3230
90	725	7250		

the reacting substances. When one of these substances is used as solvent, as in the present case, C may be regarded as constant throughout the reaction, and k_1C may be replaced by k. The latter is the velocity coefficient of Goldschmidt and Udby's equation. The true velocity coefficient $k_1 = k/C$. If C is changed by the addition of a second solvent, this fact must be taken into account when calculating k_1. In Table V, C has been taken as unity for the pure solvent.

Fig. 1 shows diagrammatically the values of k in Table V and also the results for 0·1*N*-*n*-butyric acid in mixtures of *iso*amyl alcohol and ligroin. The curves are similar in shape and appear to exhibit breaks, but this cannot be confirmed without a large number of fresh determinations. The experimental points have been joined merely to show the general trend.

Discussion of Results.

The most striking feature of these results is the large increase in the value of k_1 as the alcohol is diluted with the neutral solvent. The values of k, on the other hand, although decreasing at first and then rising, do not fluctuate to such an extent. This suggests that the method by which k_1 has been calculated from k is inaccurate, or that there is some compensating factor which has not been taken into account, for it seems unlikely that the reactivity should increase more than ten times on the addition of a second solvent.

While the assumption that the reaction velocity is proportional to the concentration of the alcohol is probably correct in the case of an uncatalysed reaction, it does not follow that the same is true in the presence of a catalyst. In the latter case, it is quite possible that the catalyst is mainly associated with the alcohol, a certain proportion of the complexes (whether ionic or molecular) being in the active condition. If a neutral solvent, particularly one in which the catalyst is comparatively insoluble, is now added, the

relation between alcohol and catalyst may be only slightly changed. In other words, the velocity may depend upon the ratio of catalyst molecules to alcohol molecules.

Consider 50 c.c. of a 0·1*N*-solution of suberic acid in 0·1*N*-amyl-alcoholic hydrogen chloride. The velocity coefficient according to Table IV is 0·056 × 2, corresponding with the presence of a certain number of active complexes. If 50 c.c. of benzene, containing the necessary amount of suberic acid to keep the concentration constant, are now added, and it is supposed that the total number of these complexes does not alter, the number in 50 c.c. will be half the original number and the velocity coefficient will be 0·056, and not 0·053 as might be expected from the fact that the catalyst concentration is now 0·05*N*. Similarly for a 10% amyl alcohol solution, the velocity coefficient for 0·05*N* catalyst would be 0·1 times its value for 0·5*N* catalyst, or approximately 0·09. This is qualitatively in agreement with observation, as may be seen in Fig. 1: curve 4 represents the figures in Table IV for the variation of velocity coefficient with acid concentration, plotted in such a way that they show the velocity coefficient calculated as above for each mixed solvent, *i.e.*, corrected so as to show the concentration with reference to the amyl alcohol. The general shape of the later part of this curve has a distinct resemblance to the corresponding portions of the esterification curves.

If this hypothesis be correct, k represents the velocity coefficient, and not k_1.

The present results show that reaction can take place rapidly in the absence of any appreciable number of ions, but they do not afford information as to the relative effect of ions and molecules.

It has so far not been possible to explain either the diminution in k on adding small quantities of benzene, or the minimum in the conductivity curves. Attempts have been made to measure the hydrogen-ion concentration, but so far they have not been successful.

It is evident that much further work is required before more definite conclusions can be drawn, and the experiments are being continued.

Summary.

1. The velocity coefficients of esterification of suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol with benzene and ligroin have been measured in the presence of hydrogen chloride as catalyst.

2. Goldschmidt and Udby's formula has been found to yield satisfactorily constant coefficients.

3. The coefficients increase very considerably on addition of

the neutral solvents, the relation between the value of the coefficient and the composition of the solution being approximately hyperbolic. A possible explanation is that the velocity depends upon the ratio of catalyst to alcohol molecules, and not upon the concentration of catalyst in the whole solution.

4. Conductivity and viscosity measurements have also been made, and it is shown that the ionisation of the catalyst is a negligible factor in determining the velocity. The conductivity of the solutions in which the reaction took place most readily was very low.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

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CCLXXIX.—*Acid and Salt Effects in Catalysed Reactions. Part X. The Hydrolysis of Ethyl Acetate with Acetic Acid as Catalyst.*

By HARRY MEDFORTH DAWSON and WILLIAM LOWSON.

IN presence of a strong acid, the rate of hydrolysis of ethyl acetate in dilute aqueous solution is determined by the difference between two reaction velocities which are proportional, respectively, to the concentration of the unhydrolysed ester and to the square of the concentration of the hydrolysed ester.

The integration of the differential equation, which takes account of the two opposed reactions, leads to a formula of very complicated type (compare Harned and Pfanstiel, *J. Amer. Chem. Soc.*, 1922, **44**, 2193), and on this account it is customary to consider the reaction as non-reversible and to replace the total initial concentration of the ester by that corresponding with the ester which has been hydrolysed when the state of equilibrium is reached.

Since the experiments to be described by us are concerned, *inter alia*, with the determination of an accurate value for the catalytic coefficient of the hydrogen ion, it has seemed necessary to inquire to what extent and under what conditions the neglect of the reverse reaction affords a constant which may be taken as a measure of the true hydrolytic coefficient k_r in the equation for the reversible charge. The latter may be written

$$dx/dt = k_r(w - x)(a - x) - k'_r x^2,$$

in which w represents the molar concentration of water and a that of the total ester in the original solution.

Since under the conditions of the experiments to be described x may be neglected in comparison with w, and k'_r may be replaced

by $K_e k_r$, where K_e is the equilibrium constant, the above equation assumes the form

$$dx/dt = k_r\{w(a - x) - K_e x^2\} \quad . \quad . \quad . \quad . \quad (1)$$

The two simplified equations which have been compared with this are

$$dx/dt = k_0 w(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$dx/dt = k_e w(a_e - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which k_0 refers to the velocity expressed in terms of the total ester concentration, and k_e is the coefficient obtained by using the concentration of ester, a_e, which has been hydrolysed at the attainment of equilibrium.

In so far as (2) and (3) may be supposed to represent correctly the reaction velocity at different stages, the three values of dx/dt may be equated. From (1) and (2) we thus obtain

$$k_0/k_r = 1 - K_e x^2/w(a - x) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and from (1) and (3)

$$k_e/k_r = (a - x)\{1 - K_e x^2/w(a - x)\}/(a_e - x) \quad . \quad . \quad (5)$$

On the assumption that k_r is the true velocity coefficient of the hydrolytic reaction, the ratios k_0/k_r and k_e/k_r show to what extent equations (2) and (3) may be used in substitution for equation (1). When the ester concentration is small, *e.g.*, $a = 0{\cdot}05$, the difference between the coefficients is not a matter of importance, but it may be readily shown that the difference is considerable for higher ester concentrations.

The comparison we have instituted has reference to the ester concentration used in our experiments, *viz.*, $a = 0{\cdot}4$; under these conditions $w = 53{\cdot}0$, and if $K_e = 4{\cdot}0$, $a_e = 0{\cdot}3886$, corresponding with 97·15% hydrolysis. The relevant numbers are shown in Table I, from which it is apparent that equation (2) yields a

TABLE I.

Comparison of Velocity Coefficients.

x	0	0·05	0·1	0·15	0·2	0·25	0·3	0·35
k_0/k_r	1·0	0·999	0·997	0·993	0·985	0·969	0·932	0·815
k_e/k_r	1·029	1·033	1·037	1·040	1·044	1·048	1·052	1·055

" constant " which in the early stages of the reaction differs very little from the true coefficient k_r. On the other hand, equation (3) gives a " constant " which is very considerably greater than k_r, and such advantage as may be claimed for this equation is limited to the circumstance that the " constant " associated with it does not change very greatly even in the late stages of the reaction.

The relations disclosed by the above comparison have been of considerable assistance in deciding that equation (2) is to be preferred to (3) as a basis for the development of an integral formula to represent the earlier stages of the hydrolysis of ethyl acetate under the catalytic influence of acetic acid.

Results obtained in the study of the acetone–iodine reaction have shown that catalytic effects are produced by the undissociated acetic acid and the acetate ion as well as by the hydrogen ion, and if these are taken into account in the present case, the form assumed by equation (2) is

$$dx/dt = \{k_h[H^+] + k_a[A^-] + k_m[HA]\}w(a - x)$$

Experiments to be described in a subsequent paper show, however, that the coefficients k_a and k_m are very small, and that the terms $k_a[A^-]$ and $k_m[HA]$ can in general be neglected in comparison with $k_h[H^+]$ when acetic acid is used as catalyst in the absence of the corresponding salt. If b denotes the original concentration of the acetic acid, then $[H^+] = \sqrt{K(b + x - [H^+])} = \text{approx.}\sqrt{K(b+x)}$, and the previous equation becomes

$$dx/dt = k_h w\sqrt{K}(a - x)(b + x)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (6)$$

$$= k(a - x)(b + x)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

By substituting $y = (b + x)^{\frac{1}{2}}$, equation (6a) becomes

$$k \,.\, dt = 2dy/(a + b - y^2)$$

which may be integrated by the method of partial fractions. We thus obtain

$$kt = \frac{1}{\sqrt{a+b}}\{\log(\sqrt{a+b} + y) - \log(\sqrt{a+b} - y)\} + \text{constant},$$

and since $y = \sqrt{b}$ when $t = 0$

$$\text{constant} = -\frac{1}{\sqrt{a+b}}\{\log(\sqrt{a+b} + \sqrt{b}) - \log(\sqrt{a} + b - \sqrt{b})\}$$

Replacing y by $(b + x)^{\frac{1}{2}}$ and transposing, we obtain

$$k = \frac{1}{t\sqrt{a+b}}\left\{\log\frac{\sqrt{a+b} + \sqrt{b} + x}{\sqrt{a+b} - \sqrt{b} + x} - \log\frac{\sqrt{a+b} + \sqrt{b}}{\sqrt{a+b} - \sqrt{b}}\right\} \quad (7)$$

This equation will be applied to experiments for which $a = 0{\cdot}4$, and $b = 0{\cdot}1$.

Preliminary observations under these conditions showed clearly that the reaction velocity increases in the early stages and this circumstance suggested a further analysis of equation (6a). By differentiation we obtain

$$dv/dx = \tfrac{1}{2}k(a - x)(b + x)^{-\frac{1}{2}} - k(b + x)^{\frac{1}{2}} \quad . \quad . \quad . \quad (8)$$

according to which the velocity passes through a maximum when $a - x = 2(b + x)$, *i.e.*, when $x = x_m = (a - 2b)/3$. If $a = nb$, x_m becomes $(n - 2)b/3$, and since this must be a positive quantity, it follows that a maximum velocity will only be obtained when the ester–acetic acid ratio is greater than 2. If $n =$ or < 2, the velocity should fall continuously as the reaction proceeds.

In terms of n and b, the initial velocity v_0 is given by

$$v_0 = knb^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and the maximum velocity, v_m, by

$$v_m = 2k\{(n + 1)b/3\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

whence for the ratio of maximum to initial velocity we obtain

$$v_m/v_0 = 2/n \, . \, \{(n + 1)/3\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

according to which this ratio depends only on n or a/b. Table II shows how the relative magnitude of the maximum velocity and the point at which it occurs depend on the value of n. The values of n, x_m, and v_m/v_0 are recorded in the first, second, and fourth horizontal lines; the third line gives the % of ester, 100 x_m/a, which has been hydrolysed when the velocity attains its maximum value.

TABLE II.

n	2·0	3·0	4·0	5·0	6·0	10·0
x_m	0	$b/3$	$2b/3$	b	$4b/3$	$8b/3$
$100x_m/a$	0	11·1	16·7	20·0	22·2	26·7
v_m/v_0	1	1·03	1·075	1·13	1·19	1·40

EXPERIMENTAL.

The velocity measurements were made at 25°. The ethyl acetate was a fractionated research chemical which on saponification was found to contain 99·9% of ester. Preliminary observations showed that greatly increased accuracy could be obtained by the use of weight-volumetric methods and that this mode of procedure was essential in so far as the determination of the average speed at successive stages of the reaction was attempted.

In the recorded experiments, a 25 (or 10) c.c. sample of the ester solution was introduced into a weighed flask containing water and a measured quantity of phenolphthalein, the flask and its contents being re-weighed before and after the addition of the 0·1*N*-sodium hydroxide necessary to produce the tint accepted as an indication of the end-point. Using every precaution, it was found that titration results were reproducible within limits of $\pm$ 0·02 c.c. The influence of the titration error on the value of x varies with the progress of the reaction, but is in all cases such as

to warrant the belief that the accuracy of the analytical procedure was sufficient for the purpose of the inquiry.

Table III gives the detailed record of an experiment the data for which have been examined in reference to equation (7). Col. 1 gives the time in minutes, col. 2 the weight of solution titrated, and col. 3 the weight of standard alkali solution (0·0996*N*-NaOH) required. Col. 4 records the values of $(b + x)$ in mols. per litre, and col. 5 gives the values of k calculated from equation (7).

TABLE III.

$a = 0·413$; $b = 0·0977$.

t (mins.).	Wt. of sol. titrated.	W. of standard alkali.	$b + x$.	$k \times 10^5$.
1,645	24·934	24·462	0·1033	2·61
5,640	24·940	25·859	0·1172	2·63
9,970	24·943	29·337	0·1326	2·61
14,300	24·951	33·206	0·1481	2·61
17,160	10·006	14·875	0·1587	2·61
25,985	10·002	15·936	0·1902	2·59
33,005	10·002	20·139	0·2158	2·60
36,030	10·016	22·741	0·2262	2·59
43,120	9·993	25·169	0·2509	2·59
50,310	10·005	27·515	0·2739	2·59
64,675	9·999	31·797	0·3167	(2·57)
74,840	9·992	34·378	0·3427	(2·56)
84,860	9·987	36·710	0·3661	(2·55)
94,950	9·993	38·715	0·3859	(2·54)
106,870	9·985	40·760	0·4066	(2·52)

In accordance with the preceding analysis (compare Table I), the value of k would be expected to remain sensibly constant until about half of the original ester has been hydrolysed. As the figures in the last column of Table III indicate, this anticipation is fully realised within the limits of experimental error. The steady fall in the later (bracketed) values of k is quite in accordance with expectation.

If the experimental data for the later stages of the reaction are to be analysed with any degree of precision, it is essential that consideration should be given to the reverse reaction, but this does not necessarily imply the use of the complex integration formula (compare p. 2107). On the contrary, if the measurements of the reaction velocity are sufficiently accurate and the variations in the velocity are relatively small, the experimental results may be tested by comparing the observed average velocity for successive time intervals with the calculated velocity for the middle of each such interval. In so far as the variation of the velocity is concerned, the reaction investigated by us fulfils the stipulated requirement until the latest stages are reached, in that the effect of diminishing ester concentration is counteracted by the effect of

increasing concentration of the acetic acid. If $\bar{v} = \Delta x/\Delta t$ is the average velocity for an interval in which x increases from x_1 to x_2, and $\bar{x} = (x_1 + x_2)/2$ represents the mean value of x, then in accordance with equation (6) we have

$$\bar{v} = k_h w\sqrt{K}(a - \bar{x})(b + \bar{x})^{\frac{1}{2}} - k'_h\bar{x}\sqrt{K}(b + \bar{x})^{\frac{1}{2}}$$

and since $$k_h w\sqrt{K} = k \text{ and } k'_h = K_e k_h$$

this may be written

$$\bar{v} = k\{(a - \bar{x})(b + \bar{x})^{\frac{1}{2}} - K_e/w \,.\, \bar{x}(b + \bar{x})^{\frac{1}{2}}\} \quad . \quad . \quad (12)$$

The application of equation (12) to the experimental data is shown in Table IV. Col. 1 gives the length of the time interval (Δt) between each successive pair of readings in Table III, col. 2 the mean concentration of the ester ($a - \bar{x}$), col. 3 the mean concentration of the acetic acid ($b + \bar{x}$), col. 4 the observed mean velocity, col. 5 the velocity calculated from equation (12) with $k = 2{\cdot}61 \times 10^{-5}$ (see Table III), whilst col. 6 gives the values of k obtained by dividing the observed average velocity by $(a - \bar{x})(b + \bar{x})^{\frac{1}{2}} - K_e/w \,.\, \bar{x}(b + \bar{x})^{\frac{1}{2}}$.

TABLE IV.

Δt (mins.).	$(a - \bar{x})$.	$(b + \bar{x})$.	$\bar{v} \,.\, 10^6$ (obs.).	$\bar{v} \,.\, 10^6$ (calc.).	$k \,.\, 10^5$.
1,645	0·4102	0·1005	3·45	3·39	2·65
3,995	0·4005	0·1102	3·48	3·47	2·62
4,330	0·3858	0·1249	3·56	3·56	2·61
4,330	0·3704	0·1403	3·58	3·62	2·57
2,860	0·3573	0·1534	3·70	3·65	2·64
8,825	0·3363	0·1744	3·57	3·65	2·55
7,020	0·3077	0·2030	3·65	3·60	2·65
3,025	0·2897	0·2210	3·44	3·52	2·55
7,090	0·2722	0·2385	3·48	3·44	2·64
7,190	0·2483	0·2634	3·20	3·28	2·55
14,455	0·2154	0·2953	2·96	2·99	2·58
10,075	0·1810	0·3297	2·58	2·62	2·56
10,020	0·1563	0·3544	2·34	2·32	2·63
10,090	0·1347	0·3760	1·96	2·03	2·52
11,920	0·1145	0·3962	1·74	1·73	2·62

In reference to the above table, it may be noted that the observations cover a period of 75 days, at the end of which about 75% of the ester had been hydrolysed. The original intention was to make the successive time intervals approximately equal, but various circumstances intervened to prevent the carrying out of this proposal. The close agreement of the observed and calculated velocities shows that the reaction proceeds throughout in accordance with the requirements of equation (12). This is further shown by the constancy of the k values in the last column.

The estimated probable error in the determination of the interval velocities is about 2% and this corresponds fairly well with the

deviations of the separate k values from the mean. The arithmetic mean of all the recorded numbers is $k = 2{\cdot}60 \times 10^{-5}$, which is almost identical with the mean value of the coefficient derived from the application of the integration formula (7) to the first half of the reaction (see Table III).

In this connexion it may be noted that equation (12) involves the assumption that the hydrogen-ion concentration is given by $[H^+] = \sqrt{K(b + \bar{x})}$. If this were replaced by the more accurate value derived from $[H^+] = \sqrt{K(b + \bar{x} - [H^+])}$, the average value of k would be increased by about 0·4%. The use of the simpler expres-

FIG. 1.

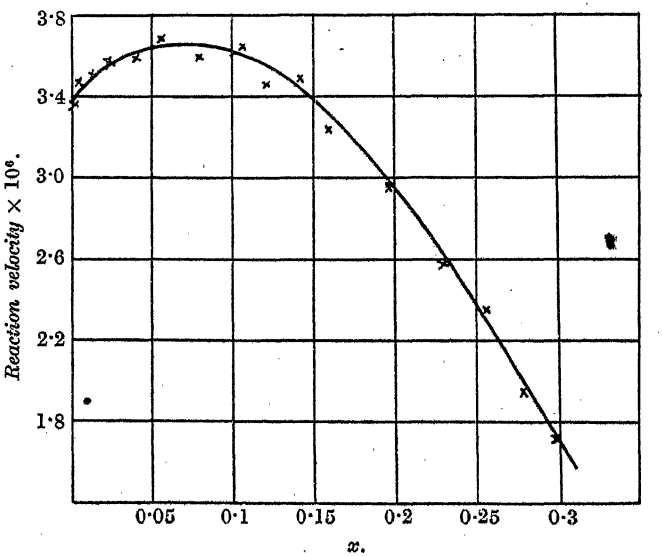


Diagram showing the variation of the reaction velocity with the proportion of ester hydrolysed.

sion is justified by the fact that the difference involved is probably within the limits of error of the mean value of k.

The observations recorded in Table IV do not actually give the initial velocity v_0. To obtain this, measurements were made with solutions for which the initial concentrations of ester and acetic acid were so adjusted that $(a - \bar{x})$ and $(b + \bar{x})$ were equal to the initial values (a and b) in the experiment of Tables III and IV. The velocity derived in this way was $v_0 = 3{\cdot}34 \times 10^{-5}$, which compares with the calculated value, $v_0 = 3{\cdot}37 \times 10^{-5}$.

The course of the reaction may be clearly visualised with the aid of the diagram. The curve on this shows the variation of the

velocity as expressed by equation (12), whilst the points represent the measured average velocities for the successive time intervals. Equations (8) and (11) give $x_m = 0{\cdot}072$ for the point at which the velocity reaches its maximum value and $v_m/v_0 = 1{\cdot}087$ for the ratio of the maximum to the initial velocity. Although direct comparison between theory and experiment is not possible, it is apparent that these numbers are in general agreement with the observed course of the reaction.

Substituting $K = 1{\cdot}85 \times 10^{-5}$ and $w = 53{\cdot}2$ in the expression $k = k_h w\sqrt{K} = 2{\cdot}61 \times 10^{-5}$, we obtain $k_h = 1{\cdot}14 \times 10^{-4}$ as the value of the catalytic coefficient for the hydrogen ion in the hydrolysis of ethyl acetate at 25°.

Summary.

An examination has been made of the extent to which the neglect of the reverse reaction interferes with the derivation of true velocity coefficients in the process of ester hydrolysis. It is shown that the usual procedure does not yield the required coefficients unless the ester concentration is very small.

Accurate measurements of the rate of hydrolysis of ethyl acetate in presence of acetic acid have been made which permit of a direct comparison of the observed and calculated velocities at successive stages of the reaction.

Under the experimental conditions (ester, 0·4 molar; acetic acid, 0·1 molar), the velocity passes through a maximum in accordance with the theoretical predictions.

The value of the catalytic coefficient obtained for the hydrogen ion at 25° is $k_h = 1{\cdot}14 \times 10^{-4}$.

THE UNIVERSITY, LEEDS. [*Received, June 7th*, 1927.]

CCLXXX.—*The Action of Hydrazines on Semicarbazones. Part III.*

By WILLIAM BAIRD and FORSYTH JAMES WILSON.

IN Part II (J., 1926, 2369) it was shown that acetophenone- and benzophenone-δ-anilinosemicarbazones on heating gave the phenylhydrazones and 4-aminourazole,* the reaction probably taking place in two stages:

$$2CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh = CO(NH{\cdot}N{:}CRR')_2 +$$
$$CO(NH{\cdot}NHPh)_2 = 2CRR'{:}N{\cdot}NHPh + CO\langle^{NH{\cdot}NH}_{N(NH_2)}\rangle CO$$

* In Part II this compound was erroneously described as 1-aminourazole; the name and formula should be as now given.

From acetophenone-δ-anilinosemicarbazone, some ketazine was also produced, probably by the thermal decomposition of the intermediate carbohydrazone (compare Brown, Pickering, and Wilson, this vol., p. 107). This interpretation of the reaction has now been confirmed by heating together diacetonecarbohydrazone and diphenylcarbohydrazide, the products being acetonephenylhydrazone, 4-aminourazole and dimethylketazine. The thermal decomposition of acetone-, pinacolin-, and benzylidene-δ-anilinosemicarbazones followed the same course, no diphenylcarbohydrazide being actually isolated. In the case of acetone-δ-diphenylaminosemicarbazone, the thermal decomposition of which conformed to the general scheme, some tetraphenylcarbohydrazide, $CO(NH\cdot NPh_2)_2$, was actually isolated.

In the expectation of obtaining δ-anilinothiosemicarbazones, the behaviour of acetone-, acetophenone-, and dibenzyl ketone thiosemicarbazones on heating with phenylhydrazine was investigated in the usual manner. In each case, however, the phenylhydrazone and thiosemicarbazide were produced, the reaction being $CRR'{:}N\cdot NH\cdot CS\cdot NH_2 + NH_2\cdot NHPh = CRR'{:}N\cdot NHPh + NH_2\cdot NH\cdot CS\cdot NH_2$. Since acetophenone- and dibenzyl ketone semicarbazones gave excellent yields of δ-anilinosemicarbazones, the thiosemicarbazide residue is evidently more easily replaced than the semicarbazide residue.

Experimental.

Thermal Decomposition of δ-Anilinosemicarbazones.—In the preparation of δ-anilinosemicarbazide hydrochloride already described, it was found more advantageous to hydrolyse the acetophenone derivative (3·3 g.) by boiling under reflux for 20 minutes with 6% hydrochloric acid (75 c.c.) and to remove the acetophenone from the hot liquid by three extractions with carbon tetrachloride. The aqueous solution on cooling deposited the hydrochloride, the remainder of which was obtained by evaporating the filtrate under reduced pressure.

Acetone-δ-anilinosemicarbazone was prepared by mixing acetone with a concentrated aqueous solution of the hydrochloride and gradually adding a slight excess of solid potassium acetate with shaking. After cooling in ice for 5 hours, the product was collected (yield 94%). It crystallises in plates, not needles as formerly described (J., 1924, **125**, 2146). The m. p. varies somewhat with the rate of heating; this preparation had m. p. 170°, which was not depressed on admixture with the specimen previously described. (Found: N, 27·1. Calc.: N, 27·2%). *Methyl ethyl ketone δ-anilino-*

semicarbazone (plates from alcohol, m. p. 137°) was prepared in the same way (Found: N, 25·4. $C_{11}H_{16}ON_4$ requires N, 25·4%).

Acetone-δ-anilinosemicarbazone was heated at 180° for 5 hours in a distillation flask with occasional evacuation until distillation ceased. The small quantity of distillate, after hydrolysis with dilute hydrochloric acid, yielded acetone on fractionation; the remainder of the liquid gave with benzaldehyde and potassium acetate a mixture of benzaldehydephenylhydrazone and benzalazine. The semi-resinous product remaining in the reaction flask was extracted with boiling absolute alcohol, which left a residue of 4-aminourazole. The alcoholic extract would not crystallise, but gave the usual diphenylcarbohydrazide colour reactions. Hence the products were acetonephenylhydrazone, dimethylketazine, and 4-aminourazole.

An intimate mixture of diacetonecarbohydrazone and diphenylcarbohydrazide (molecular quantities) was heated under the same conditions as before. The products were again acetonephenylhydrazone, dimethylketazine, and 4-aminourazole.

Pinacolin-δ-anilinosemicarbazone. The thermal decomposition was effected exactly as before. The distillate contained pinacolinphenylhydrazone and pinacolinazine, identified as such by hydrolysis with acid. The residue in the flask contained 4-aminourazole and gave the colour reactions of diphenylcarbohydrazide, which, however, could not be isolated.

Pinacolinazine was prepared by refluxing 11 g. of the ketone with 2·5 g. of hydrazine hydrate in 10 c.c. of absolute alcohol for 2 hours. After evaporation of the solution, the residual oil was dried over potassium carbonate and distilled; it was an almost colourless oil, b. p. 213—216°, 103°/17 mm., smelling somewhat like acetamide, insoluble in water and easily hydrolysed on boiling with acid (yield 77%) (Found: N, 14·3. $C_{12}H_{24}N_2$ requires N, 14·3%).

Benzylidene-δ-anilinosemicarbazone was heated for 1 hour at 230°. Since benzaldehydephenylhydrazone decomposes at about this temperature, the reaction was carried out under reduced pressure in a flask of the Anschütz type, in the collar of which a distillate, which soon solidified, collected. The whole reaction mass was extracted with boiling absolute alcohol; benzaldehydephenylhydrazone passed into solution whilst 4-aminourazole, the only other product, remained undissolved.

Acetone-δ-diphenylaminosemicarbazone. The reaction was carried out as usual: 4 hours' heating at 190—195°. The distillate on hydrolysis with hydrochloric acid gave acetone, diphenylhydrazine hydrochloride, and hydrazine hydrochloride. The dark residue in the flask was extracted with boiling absolute alcohol and then with

boiling water; the alcoholic extract on concentration deposited small needles of tetraphenylcarbohydrazide (Acree, *Ber.*, 1903, **36**, 3157) (Found: N, 14·4, 14·3. Calc.: N, 14·2%), and evaporation of the aqueous extract left 4-aminourazole. The products were therefore acetonediphenylhydrazone, dimethylketazine, 4-aminourazole, and tetraphenylcarbohydrazide.

Action of Phenylhydrazine on Thiosemicarbazones.—Molecular quantities of the reactants were heated in toluene solution or suspension at 135°.

Acetonethiosemicarbazone (6½ hours). A little ammonia was evolved, but the only products isolated were thiosemicarbazide, acetonephenylhydrazone, and a little unaltered substance.

Acetophenonethiosemicarbazone (5 hours). This compound dissolved completely and after some time thiosemicarbazide began to separate; some hydrogen sulphide and ammonia were evolved. The substances isolated were thiosemicarbazide, acetophenonephenylhydrazone, and a small quantity of an orange-coloured *substance*, m. p. 171—172°.

Dibenzyl ketone thiosemicarbazone (which crystallises in silvery leaves, m. p. 165—166°, from alcohol or benzene), was obtained by refluxing 2·1 g. of the ketone in 15 c.c. of alcohol with 0·9 g. of thiosemicarbazide in the minimum quantity of hot water for ¾ hour (Found: N, 14·9. $C_{16}H_{17}N_3S$ requires N, 14·8%). The reaction with phenylhydrazine (4 hours) gave thiosemicarbazide, dibenzyl ketone phenylhydrazone, and some unaltered substance only.

In conclusion, we wish to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the cost of this work. We wish also to thank the Governors of this College for a research assistantship which has enabled one of us (W. B.) to share in the investigation.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

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CCLXXXI.—*The Systems* B_2O_3–SO_3–H_2O *and* B_2O_3–P_2O_5–H_2O.

By MIRIAM LEVI and LIONEL FELIX GILBERT.

(i) *The System* B_2O_3–SO_3–H_2O.

MERZ (*J. pr. Chem.*, 1866, **99**, 81) stated that when equal weights of boric and concentrated sulphuric acids were heated to constant weight at 250—280° a substance was obtained of composition $5B_2O_3,2SO_3,2H_2O$. Gmelin reported (*Ann. Supp.*, 1867, **5**, 169),

that boron trioxide and boric acid dissolved extensively in concentrated sulphuric acid on heating, and that on cooling a thick syrup was obtained which deposited hydrates of boric acid on standing in moist air. Schultz-Sellack (*Ber.*, 1871, **4**, 12) found that the solution of boric acid in concentrated sulphuric acid gave on evaporation a viscous or glassy mass, which was not of constant composition. If, however, the sulphuric acid solution was treated with sulphur trioxide, or if boron trioxide was added to fuming sulphuric acid, leafy crystals, of composition $B_2O_3,3SO_3,H_2O$, were obtained on evaporation.

D'Arcy (J., 1889, **55**, 155) could not confirm the existence of Merz's or Schultz-Sellack's compounds. He reports that on mixing boric acid with excess of sulphur trioxide a violent reaction occurs; on heating the mixture at 100° till no more fumes are evolved and then cooling, a white substance separates of composition $B_2O_3,6SO_3,3H_2O$. Herz (*Z. anorg. Chem.*, 1903, **34**, 205) has made solubility measurements of boric acid in four different concentrations of sulphuric acid, 9*N* being the highest; no examination of the solid phases was made.

In the present work, a partial survey of the condensed ternary system has been made at 25° and 45° by the Schreinemakers method, supplemented by direct analyses of the solid phases. None of the above compounds has been found to exist under our experimental conditions, but the new compounds $B_2O_3,SO_3,4H_2O$ and $3B_2O_3,SO_3,3H_2O$ appear to be definitely characterised.

The reactants supplying the components were, in addition to water, concentrated sulphuric acid, fuming sulphuric acid, boric acid, and a specimen of powdered boron trioxide containing about 13% of water. These substances were in each case of a satisfactory degree of purity.

The boric–sulphuric acid mixtures examined were analysed by Herz's method (*Z. anorg. Chem.*, 1903, **33**, 353), which was tested and found to be very accurate, although the few solubilities recorded by that author do not agree with ours (see below), possibly owing to the fact that in determining them he used a less accurate method (compare Kendall and Andrews, *J. Amer. Chem. Soc.*, 1921, **43**, 1550). The procedure was to titrate suitably diluted solutions with 0·1*N*-sodium hydroxide in the presence of *p*-nitrophenol as indicator until the first yellow colour appeared, corresponding with the neutralisation of the sulphuric acid; 10 c.c. of a neutral, saturated solution of mannite and two drops of phenolphthalein solution were then added, and the titration was continued until a definite pink colour persisted for 3 minutes. This latter amount of alkali was equivalent to the boric acid present.

The solubility determinations were complicated, when high concentrations of sulphuric acid were concerned, by the ease with which highly supersaturated solutions were obtained, even when solution was effected at room temperatures. This tendency was especially marked in the region relating to the solid phase, $B_2O_3,SO_3,4H_2O$.

In some cases, solutions stood for several weeks before any solid phase commenced to separate, and the further precipitation was also very slow. None of the usual methods for overcoming this type of difficulty, *viz.*, cooling, heating, or the addition of foreign bodies or of the appropriate solid phase, seemed to have any marked effect.

Three methods of obtaining the necessary data for the ternary diagram were employed.

(*a*) The well-known method of agitating in a thermostat sealed glass tubes containing the reactants mixed in suitable proportions was employed for low concentrations of sulphuric acid, where equilibrium was easily attained. As soon as a tube was opened, the liquid and the wet solid were rapidly sampled and the samples were transferred to a specific-gravity bottle in the thermostat and to a weighing bottle, respectively.

(*b*) The reactants were stirred with dry air in an apparatus similar to that used by Donnan and White (J., 1911, **99**, 1788), the Gooch crucible used by these authors for separating solid and liquid being here replaced by a glass filter-funnel with a permanently fixed filter-plate of fritted glass. This method was used with some of the higher concentrations of (non-fuming) sulphuric acid, where the attainment of equilibrium was too slow by the tube method.

(*c*) The reactants were placed in a glass bottle of about 500 c.c. capacity, fitted with a glass stirrer passing through a mercury seal. After long stirring, the solid was allowed to segregate and samples of liquid and solid were taken. This method was used for mixtures containing fuming sulphuric acid, and for some other mixtures of high viscosity.

Compositions of saturated solutions and of their respective wet solids are shown in Table I and Fig. 1 for 25°, and in Table II for 45°. Although Herz's solubilities were determined at 26°, they are consistently lower than our values for 25°; *e.g.*, the concentration of boric acid in 8·75*N*-sulphuric acid is 0·092*N* (Herz) and about 0·37*N* by interpolation from our results. Areas corresponding to three distinct solid phases will be observed in Fig. 1, *viz.*, $B_2O_3,3H_2O$ (*i.e.*, H_3BO_3), $B_2O_3,SO_3,4H_2O$, and $3B_2O_3,SO_3,3H_2O$, but there is no evidence here for any of the ternary compounds described by other authors. On plotting the 45°-data, a similar

Table I.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d_4^{25°}$.	SO_3.	B_2O_3.	SO_3.	B_2O_3.	Solid phase.
1·017	0·00	3·08*			
1·032	1·96	2·87	0·70	35·76	
1·039	2·90	2·79			
1·088	9·12	2·18	4·82	28·82	
1·112	11·85	2·00			
1·160	17·56	1·54			
1·270	28·82	1·04			
1·284	30·62	0·97	19·90	20·26	
1·305	32·78	0·87	18·94	24·78	
1·412	41·78	0·71	30·33	15·98	H_3BO_3.
1·446	44·44	0·68	27·74	21·60	
1·479	46·80	0·65	26·68	24·84	
	53·94	1·46	3·89	52·19	
	54·89	1·47			
1·625	55·84	2·69	47·22	10·79	
	54·66	6·09			
	54·16	7·17	35·30	23·98	
1·668	53·50	8·12	37·80	22·30	
	55·74	7·70	45·03	20·01	
1·617	54·73	10·32	48·19	17·76	
	54·20	11·73			$B_2O_3,SO_3,4H_2O$.
	51·87	15·45	49·34	18·02	
	47·27	20·93			
	51·87	21·85			
	52·89	21·06	38·72	40·64	
	57·32	18·34	41·47	38·54	
	61·44	16·07	43·71	37·34	
	63·36	15·23			
	70·02	12·00	52·61	30·05	$3B_2O_3,SO_3,3H_2O$
1·882	73·66	10·39	59·50	24·90	
	86·24	5·07			
	86·50	4·96			
	87·72	4·82	43·43	43·45	

* In agreement with Kendall and Andrews (*loc. cit.*).

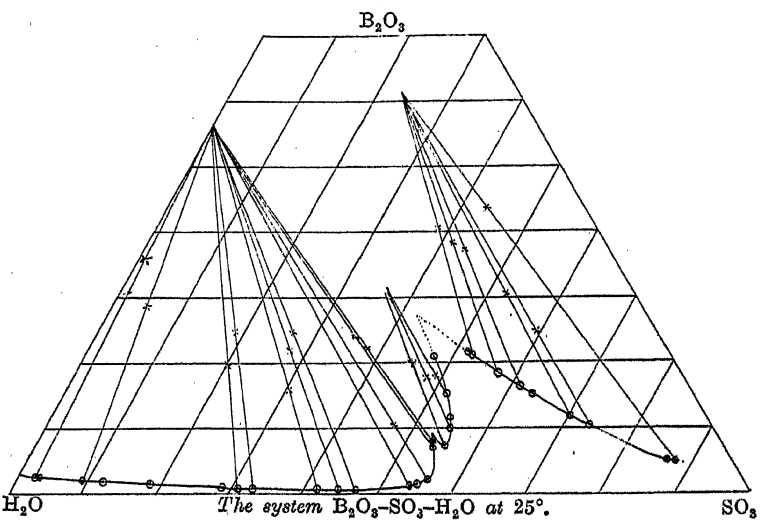
Table II.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d_4^{25°}$.	SO_3.	B_2O_3.	SO_3.	B_2O_3.	Solid phase.
1·023	0·00	5·17			
1·029	0·47	5·07	0·13	38·37	
1·036	1·93	4·83	0·71	34·57	
1·086	8·58	3·74	4·86	28·88	
1·097	10·18	3·51	5·78	26·54	H_3BO_3.
1·231	25·48	1·89	15·48	23·33	
1·446	44·87	0·13	33·73	13·98	
1·628	52·25	7·07	37·81	20·52	
1·671	54·13	8·33	45·45	19·83	
1·685	56·65	6·14	49·50	15·21	
	60·89	4·89	49·49	17·89	$B_2O_3,SO_3,4H_2O$.
	62·66	6·85	47·35	21·05	
1·800	57·22	13·56			
	59·87	23·60	41·08	35·18	
	57·70	19·25	41·34	40·29	$3B_2O_3,SO_3,3H_2O$.
	60·43	17·99	46·64	35·66	

solubility curve to that at 25° is obtained, but the tie-lines corresponding to the two new compounds are not so satisfactorily convergent. The attainment of equilibrium was too slow for more satisfactory data to be obtained, but it is considered that there is little doubt that the above compounds are also obtained at 45°. The quite characteristic appearances of the solid phases were also similar to those obtained at 25°.

Samples of the two new solids, prepared by the interaction of boric acid with 88% sulphuric acid, and of boron trioxide (87%)

FIG. 1.



The system B_2O_3–SO_3–H_2O *at* 25°.

with concentrated sulphuric acid, respectively, and kept in desiccators on carefully dried porous plates, gave the following analyses:

	$B_2O_3,SO_3,4H_2O$.				$3B_2O_3,SO_3,3H_2O$.			
	I.	II.	III.	Calc.	I.	II.	III.	Calc.
% SO_3	36·6	36·1	36·6	36·0	22·1	25·4	24·9	23·3
% B_2O_3	31·2	32·3	32·0	31·5	64·8	61·9	59·5	61·0

It is considered that discrepancies between observed and calculated results can fairly be ascribed to a certain amount of hydrolysis which may have occurred on sampling, and also to the difficulty of draining the viscous adherent liquids, the viscosity of which is especially high in the case of the second compound.

$B_2O_3,SO_3,4H_2O$ is a white, finely-divided, crystalline substance; $3B_2O_3,SO_3,3H_2O$ consists of larger, colourless crystals. Both compounds rapidly absorb moisture from the atmosphere, with consequent decomposition.

Viscosities of Solutions of Boric Acid in Concentrated Sulphuric Acid.—A few determinations were made at 25° of the viscosities of solutions of boric acid in concentrated sulphuric acid compared with that of the solvent, by the capillary flow method. No great accuracy is claimed for these measurements, which, however, help to emphasise some of the difficulties experienced when working with this system. The results obtained were:

% H_3BO_3	0	8·5	15·9	24·5	30·0	37·6	42·7
Relative time of flow	1	3·96	12·5	40·1	84·0	219	440

(ii) *The System* B_2O_3–P_2O_5–H_2O.

Vogel (*Z. anal. Chem.*, 1870, **9**, 376) obtained a compound containing "an equal number of equivalents of boric and phosphoric acids" by strongly heating mixtures of these substances. Meyer (*Ber.*, 1889, **22**, 2919), Mylius and Meusser (*Ber.*, 1904, **37**, 397), and Prescher (*Arch. Pharm.*, 1904, **242**, 199) all obtained a substance of empirical composition BPO_4 by methods similar to that of Vogel, whose compound, therefore, was probably the same (compare Comey, "Dictionary of Chemical Solubilities," 1921, p. 668). BPO_4, thus prepared, is insoluble in water and only slowly decomposed by boiling alkalis. Mylius and Meusser observed, however, that, when formed at comparatively low temperatures (80—100°) from the above reactants, or from solutions of metaboric acid in acetic and phosphoric acids or from solutions of boric acid in phosphoric and concentrated sulphuric acids, BPO_4 is soluble in water with decomposition, but becomes insoluble on heating to 400°. Gustavson (*Ber.*, 1871, **4**, 975) made BPO_4 by heating boron trioxide with phosphorus pentachloride, and boron trichloride with phosphorus pentoxide. Apparently here, too, the soluble compound was first formed and became insoluble on further heating.

The ternary system B_2O_3–P_2O_5–H_2O at 25° has now been partially investigated, and BPO_4 occurred as the solid phase in one of the regions under examination.

Well-boiled syrupy phosphoric acid, free from phosphorous acid, was employed as the source of phosphorus pentoxide, and was suitably diluted as required. The boric acid and boron trioxide used were similar specimens to those mentioned previously.

On examination of the literature, Kolthoff's method (*Chem. Weekblad*, 1922, **19**, 449) appeared to be the most suitable for the rather difficult determination of mixtures of boric and phosphoric acids, but it was found not to give sufficiently accurate results. In addition to the difficulty of distinguishing between various shades of pink, it was found that the titration value for the phosphoric acid end-point varied with the amount of boric acid present

if the titration was carried on until the same p_H value was obtained in each case. Whilst retaining the use of sodium citrate and Kolthoff's p_H value for the total-acid end-point, which was found to be correct and unaffected by the relative amounts of the acids, a new procedure was adopted. 0·1*N*-Mixtures of known composition of boric and phosphoric acids were made up, 10 c.c. of 40% sodium citrate solution and thymol-blue were then added, followed by the appropriate amount of 0·1*N*-sodium hydroxide to convert all the phosphoric acid to the secondary sodium salt. The p_H numbers acquired by the solutions were then determined by comparison with a colour chart, and plotted against the % of boric acid molecules in the total acid molecules present.

The correction graph was plotted from the following data, of which the accuracy is considered sufficient for the purpose :

% H_3BO_3.....	100	96	82	70·5	58	52	40·5	35	26·3	15·5	0
p_H	8·2	8·3	8·4	8·5	8·6	8·7	8·8	8·9	9·0	9·1	9·2

In the analysis of an unknown mixture the % of boric acid was first determined roughly and the corresponding p_H number read off the graph. Exact determinations were then made on 25 c.c. of another sample by titrating with caustic soda (in presence of sodium citrate and thymol blue) to this p_H number, thus allowing the amount of phosphoric acid to be calculated; 10 c.c. of a saturated solution of mannite were then added and the solution was titrated until the colour corresponding to p_H 8·7 lasted for at least a minute. This latter volume of sodium hydroxide was equivalent to the boric acid present. A test of the method over a wide range of relative concentrations of the acids indicated that it gave very accurate results.

The first two methods employed in the preceding system were found suitable for obtaining the solubility and wet-solid data. Some difficulty was experienced in filtering satisfactorily mixtures made with high concentrations of phosphoric acid. Large quantities of boric acid and boron trioxide will dissolve in such phosphoric acid solutions with the formation of clear liquids from which a new, very finely divided, solid phase slowly separates. This coagulates slightly and settles after 3 or 4 days, but still passes through filters of average pore diameter 35—40 $\times$ 10^{-4} and in some cases even 4—5 $\times$ 10^{-4} cm.

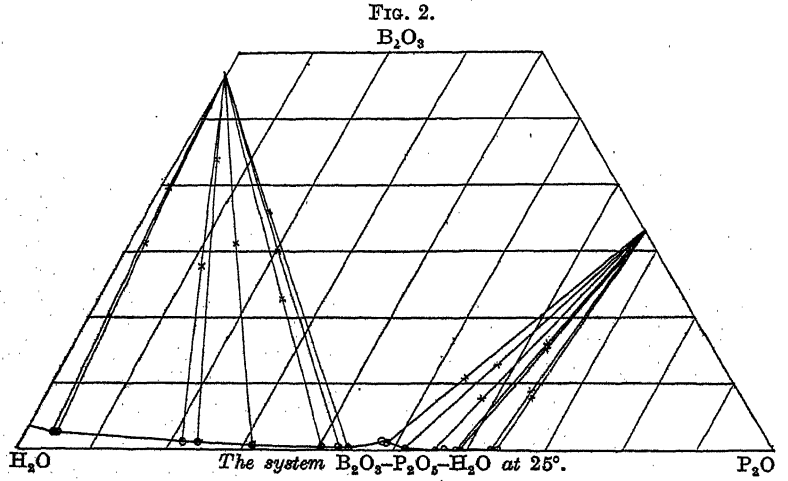
The results obtained are shown in Table III and partly in Fig. 2. The solid phase in equilibrium with solutions containing up to about 48% of P_2O_5 is boric acid, after which BPO_4 or some polymeride is formed. The BPO_4 thus obtained is the water-soluble variety. Attempts to prepare a pure dry specimen have so far

TABLE III.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d_4^{25°}$.	P_2O_5.	B_2O_3.	P_2O_5.	B_2O_3.	Solid phase.
1·042	3·63	2·55	1·23	39·80	H_3BO_3.
1·048	4·34	2·53	2·04	31·35	
1·190	21·51	1·12	11·09	27·91	
1·215	23·66	1·05	5·39	43·86	
1·281	31·01	0·62	14·10	31·03	
1·391	40·39	0·45	24·28	22·89	
	42·60	0·68	20·13	30·03	
1·434	43·70	0·68	16·11	35·78	
1·504	48·08	1·27	45·62	13·59*	
1·516	48·51	1·20			
	48·89	1·11	54·43	10·49	BPO_4.
	51·52	0·23	57·81	12·70	
	55·37	Concentration too low to be titrated.	58·12	7·50	
	56·99				
	58·35		62·73	15·9	
1·645	58·68		62·81	15·02	
	62·81		64·06	8·95	
1·722	63·43		64·40	7·94	

* Apparently point of inversion.

FIG. 2.



The system B_2O_3–P_2O_5–H_2O *at* 25°.

been unsuccessful. BPO_4 retains the viscous supernatant liquid very strongly and is rapidly attacked by atmospheric moisture. It appears to be a white, finely-divided powder.

THE WILLIAM RAMSAY INORGANIC AND PHYSICAL CHEMISTRY LABORATORIES, UNIVERSITY COLLEGE, LONDON.

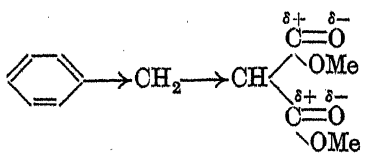
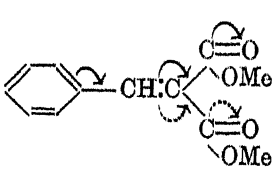
[*Received, June 7th*, 1927.]

CCLXXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXI. The Directive Influence of the Groups* $-CH_2\cdot CH(CO_2Me)_2$, $-CH{:}C(CO_2Me)_2$, $-C(CO_2Me){:}CH_2$, *and* $-CH{:}CH\cdot CH{:}C(CO_2Me)_2$ *in Aromatic Substitution.*

By JOHN WILLIAM BAKER and ALFRED ECCLES.

IT has already been shown (Baker and Wilson, this vol., p. 842) that mechanisms depending on complete co-valency changes between the side-chain and the benzene nucleus probably play, at the most, a subsidiary part in the propagation of meta-orienting influences. Thus, electron attraction due to the integral positive charge on the nitro-group is more readily propagated to the nucleus in the ω-nitroethyl than in the corresponding ω-nitrovinyl side-chain. In the present communication, an attempt is made to confirm the previous conclusion by a study of the nitration of the analogous compounds, methyl benzylmalonate (I) and methyl benzylidenemalonate (II), in which the *gem*-dicarbomethoxyl grouping replaces the nitro-group of the previous cases. On the view that the meta-orienting influence of the carboxyl group is due to the presence of a permanent fractional dipole in the resting state of the group (Baker and Ingold, this vol., p. 832), it is to be expected that the effects produced would be much smaller in magnitude than those due to the integral dipole charge on the nitro-group.

Again, however, on any mechanism of meta-substitution which depends on the alternation of single and double bonds, a larger proportion of meta-nitration should occur in the unsaturated compound (II), in which there is an unbroken conjugated system extending from the polar group throughout the nucleus, than in the corresponding saturated compound (I). Actually, in confirm-

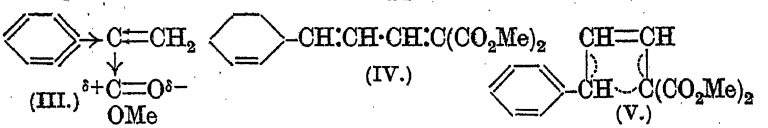
(I.)  (II.) 

ation of previous results, we find the reverse to be the case, since, on nitration, methyl benzylmalonate yields 8% of meta-derivative, whilst methyl benzylidenemalonate yields only 3%.* Thus, here

* This value is somewhat higher than that expected (1—2%). It is possible that addition of nitric acid to the double bond precedes nitration and slightly increases the proportion of meta-isomeride produced.

also the electron attraction due to the fractional positive charge on the carboxyl groups is neutralised in passing through the field of the double bond.

As in the case of the nitro-compounds previously studied, the possibility of the double linking itself acting as a dominating electron-source towards the nucleus was negatived by a study of the nitration of methyl atropate (III), in which the double bond is no longer in the path of transmission from the (single) carbomethoxyl group. We find that, on nitration, this ester yields about 5% of meta-isomeride, although, owing to the small amount of material available, the figure must be considered as approximate only.



One other case was investigated, *viz.*, that of methyl cinnamylidenemalonate (IV). The point of interest here is that there might be the possibility of valency tautomerism in the side-chain leading to the cyclic form (V), in which electron-strain might conceivably be transmitted to the nucleus through two carbon atoms only, *via* the $\alpha : \delta$ partial valency, and the proportion of *m*-isomeride produced might then be more or less comparable with that obtained on nitration of methyl benzylmalonate. Actually, however, we find no evidence of this type of transmission, since the proportion of *m*-isomeride produced is less than 1%. The electron attraction of the carbomethoxyl group is thus completely neutralised by the fields of the unsaturated chain in (IV).

Experimental.

A. *Preparation of Materials.*

Methyl Benzylidenemalonate.—This was obtained by the condensation of benzaldehyde and methyl malonate, as described by Claisen and Crismer for the ethyl ester (*Annalen*, 1883, **218**, 132; compare Liebermann, *Ber.*, 1894, **27**, 289). The product had b. p. 174—177°/15 mm., m. p. 41° (Found: C, 65·6; H, 5·5. Calc.: C, 65·4; H, 5·5%).

The methyl *o*-, *m*-, and *p*-nitrobenzylidenemalonates were obtained by the condensation of the appropriate nitrobenzaldehyde with methyl malonate in the presence of piperidine as a condensing agent (compare Knoevenagel, *Ber.*, 1898, **31**, 2593).

Methyl p-*Nitrobenzylidenemalonate.*—A mixture of *p*-nitrobenzaldehyde (7·6 g.), methyl malonate (6·6 g.), and two drops of piperidine was heated to 60° for 6 hours. On cooling, the mixture

solidified, and the *nitro-ester* was recrystallised from hot alcohol; needles, m. p. 136—137° (Found: C, 54·4; H, 4·2. $C_{12}H_{11}O_6N$ requires C, 54·3; H, 4·2%). The yield is quantitative.

Methyl m-*nitrobenzylidenemalonate*, prepared similarly but in smaller yield from *m*-nitrobenzaldehyde, has m. p. 99—100° (Found: C, 54·2; H, 4·2%).

Methyl o-*nitrobenzylidenemalonate*, m. p. 65—66° (Found: C, 54·3; H, 4·3%).

Methyl benzylmalonate was prepared by esterification of the pure acid with methyl alcohol and hydrogen chloride.

Methyl o-*Nitrobenzylmalonate*.—*o*-Nitrobenzylmalonic acid (Reissert, *Ber.*, 1896, **29**, 644) was esterified through its silver salt. The *methyl* o-*nitrobenzylmalonate* was obtained as a pale yellow, viscous oil, which did not solidify on cooling to −10°, and could not be purified by distillation (Found: C, 53·8; H, 5·1. $C_{12}H_{13}O_6N$ requires C, 53·9; H, 4·9%). On oxidation with boiling 2% permanganate, it gave an acid product contaminated with gummy material in 73·3% yield (calculated as *o*-nitrobenzoic acid). By crystallisation from ether, this was shown to contain *o*-azoxybenzoic acid. Reissert (*loc. cit.*) records the formation of the latter compound by the oxidation with permanganate of 1-hydroxyindole-2-carboxylic acid formed from *o*-nitrobenzylmalonic acid by the action of potash.

Methyl m-*Nitrobenzylmalonate*.—To a solution of 4·6 g. of sodium in 50 g. of methyl alcohol, 26·4 g. of methyl malonate were added, quickly followed by a saturated solution of 17·15 g. of *m*-nitrobenzyl chloride in methyl alcohol; the mixture was heated on the steam-bath for ½ hour and filtered from sodium chloride and the *methyl di*-m-*nitrobenzylmalonate* formed as a by-product. The salt was extracted with cold water, and the dried residue crystallised from benzene; m. p. 162—162·5° (Found: C, 56·9; H, 4·6. $C_{19}H_{18}O_8N_2$ requires C, 56·7; H, 4·5%). The alcoholic mother-liquor was concentrated, poured into water, and extracted with ether. After drying the extract and evaporating the ether, the excess of methyl malonate was separated by distillation under reduced pressure. The residue, which cannot be distilled without decomposition, was dissolved in alcohol, and the solution saturated with ammonia. After standing for several days, m-*nitrobenzylmalonamide* separated as a flocculent precipitate. After several crystallisations from water, it had m. p. 203° (Found, by microcombustion: C, 51·0; H, 4·4. $C_{10}H_{11}O_4N_3$ requires C, 50·6; H, 4·6%). The amide was hydrolysed by heating at 100° with a slight excess of 10% caustic soda. On acidification of the cooled solution, m-*nitrobenzylmalonic acid* separated, and after crystallisation from water it had m. p. 164° (decomp.) (Found, by

combustion: C, 50·5; H, 4·0. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8%). A further small quantity of the acid may be obtained by extracting the mother-liquors with ether. The yield of recrystallised acid was 2 g. Conversion of the crude methyl *m*-nitrobenzylmalonate into the amide is necessary, as treatment of the ester itself with alcoholic potash yields a very tarry product. The *m*-nitrobenzylmalonic acid was esterified through its silver salt, and *methyl* m-*nitrobenzylmalonate* obtained as a pale yellow, viscous oil, which did not solidify on cooling to −10° (Found: C, 54·2; H, 5·1%). On oxidation with boiling 2% potassium permanganate, it gave *m*-nitrobenzoic acid, m. p. 139°, in 90% yield.

Methyl p-*nitrobenzylmalonate*, m. p. 82·5—83·5° (Found: C, 53·85; H, 5·0%) was isolated from the reaction products by crystallisation from methyl alcohol (compare Section C). On oxidation, it gave *p*-nitrobenzoic acid, m. p. 237—239°, in 99% yield.

Methyl Cinnamylidenemalonate.—This was obtained by esterification of the acid (compare Liebermann, *Ber.*, 1895, **28**, 1439) by the method of Thiele and Meisenheimer (*Annalen*, 1899, **306**, 253) and had m. p. 67° (Found: C, 68·1; H, 5·9. Calc.: C, 68·3; H, 5·7%).

The isomeric nitro-derivatives were prepared by condensation of the appropriate nitro-cinnamaldehyde with methyl malonate in the presence of piperidine.

Methyl m-*Nitrocinnamylidenemalonate.*—A mixture of 8·85 g. of *m*-nitrocinnamaldehyde (Kinkelin, *Ber.*, 1885, **18**, 484), 6·6 g. of methyl malonate, and two drops of piperidine was heated to 60—70° for 5 hours. The cooled mixture, when treated with a few c.c. of ether and scratched, partly solidified. The separated crystals were washed with ether, recrystallised from alcohol, and obtained as felted needles, m. p. 125—126° (Found: C, 57·9; H, 4·6. $C_{14}H_{13}O_6N$ requires C, 57·7; H, 4·5%). The yield was small (about 15%). On oxidation with potassium permanganate, it gave *m*-nitrobenzoic acid, m. p. 129—132° (mixed m. p. 136—139°) in 76% yield.

Methyl o-*nitrocinnamylidenemalonate*, obtained in a similar manner from *o*-nitrocinnamaldehyde, and crystallised from methyl alcohol, had m. p. 114° (Found, by micro-combustion: C, 57·7; H, 4·6%). On oxidation it gave *o*-nitrobenzoic acid, m. p. 133—137° (mixed m. p. 139—141°), in 80% yield.

Methyl p-*nitrocinnamylidenemalonate* has m. p. 146—147° after crystallisation from methyl alcohol (Found: C, 57·8; H, 4·7%). On oxidation it gave *p*-nitrobenzoic acid, m. p. 229—231°, in 77% yield.

Methyl Atropate.—Tropic acid was converted into atropic acid by

the method of Hesse (*J. pr. Chem.*, 1901, **64**, 287), who, however, gave no details. The tropic acid (10 g.) was refluxed with 60 c.c. of a 50% aqueous solution of potassium hydroxide for 40 minutes, the solution extracted with ether, acidified with hydrochloric acid, and again extracted with ether. The crude atropic acid obtained from this dried ethereal extract was purified by crystallisation (twice) from dilute alcohol. The acid (4·5 g.) was dissolved in a large volume (1200—1500 c.c.) of very dilute ammonia solution, boiled to expel the excess of ammonia, and a slight excess of a hot solution of silver nitrate added. On cooling, the silver salt crystallised out, and was filtered and washed in succession with water, alcohol, and ether. Treatment of the dry silver salt with an excess of methyl iodide yields the *methyl atropate* in an almost pure state as a colourless, mobile liquid, b. p. 95—98°/6 mm. (Found: C, 73·6; H, 6·2. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2), which polymerises on keeping.

B. *Conditions of Nitration.*

In all cases, the ester was slowly added at the rate of 1—2 g. per hour to about 10 times its quantity of nitric acid (*d* 1·49) at −15— −10°. Isolation of the product was effected by pouring on crushed ice, exactly neutralising the solution, first with 10% sodium hydroxide solution and finally with sodium carbonate solution, filtering off any solid product, and extracting the mother-liquors with ether. Special precautions were necessary in the case of methyl cinnamylidenemalonate (see Section C).

C. *Details relating to Individual Cases and Determination of the Proportions of the Isomerides formed.*

Since the methods employed in the separation of the isomerides are those which have been described in detail in earlier papers in this series, details of procedure are omitted in the following pages.

Nitration of Methyl Benzylmalonate.—In this case, it was found that the yield of mixed acids obtained by oxidation of the nitration mixture was only about 80—85% of that calculated from the percentage oxidation yields of the pure isomerides (compare Section A) and their estimated relative proportions. This may be due to the *o*-nitrobenzylmalonate being converted into an indole derivative under the influence of alkali (Reissert, *loc. cit.*; compare p. 2127). The proportion of *m*-nitro-ester in the nitration mixture, as calculated from the quantity of *m*-nitrobenzoic acid isolated, is probably too low, since the total oxidation yield is less than the calculated yield, but it is still considerably greater than that present in the nitration of the benzylidenemalonate. The authors are of the opinion that the percentage of *m*-nitrobenzoic acid isolated from

the mixed acids obtained on oxidation represents fairly closely the proportion of meta-derivative formed by nitration. The presence of the azoxybenzoic acid did not interfere with the separation of the mixed acids, except that sometimes it was found necessary to crystallise the *p*-acid from water.

(Expt. 31.) The yield of mononitro-compounds was 93% (Found: C, 53·4; H, 4·9. Calc. for $C_{12}H_{13}O_6N$: C, 53·9; H, 4·9%), a further 2% of the material being accounted for as acid products produced by oxidation. On oxidation, the mixed nitro-compounds yielded acids in 70% yield, which on separation by the usual method gave nitrobenzoic acids thus: para-, m. p. 234° (either alone or mixed), 70·4%; meta-, m. p. 128—135° (mixed m. p. 141°), 7·5%; ortho- (by difference), 22·1%.

A second portion of the same nitration product was crystallised from methyl alcohol, whereby 58·8% of practically pure methyl *p*-nitrobenzylmalonate, m. p. 82°, was isolated. On oxidation of the residue, some accidental loss occurred and only a 64% yield of mixed nitrobenzoic acids was obtained; these comprised: para-, m. p. 220—223°, 30%; meta-, m. p. 124—127° (mixed m. p. 138°), 16·5%. Hence the composition of the whole nitration mixture was: para-, 71·3%; meta-, 6·8%; ortho- (by difference), 21·9%.

(Expt. 33.) The yield of mono-nitration products was 93% (Found: C, 54·2; H, 4·9%), from which 56% of pure methyl *p*-nitrobenzylmalonate was isolated by crystallisation. The residues gave a mixture of acids (*M*, by titration, 165) in 72% yield, which on separation was found to contain: para-, m. p. 233—235°, 19·2%; meta-, m. p. 123—128° (mixed m. p. 133—137°), 20·9%; ortho- (by difference), 59·9%; whence the composition of the nitration mixture was: para-, 64%; meta-, 9%; ortho- (by difference), 27%.

(Expt. 34.) The yield of mono-nitration product was 95% (Found: C, 53·3; H, 4·9%), which on oxidation gave a mixture of nitrobenzoic acids (*M*, by titration, 169) in 77% yield; this on separation was found to contain: para-, m. p. 210—215° (mixed m. p. 227—229°), 68·6%; meta-, m. p. 122—125° (mixed m. p. 135—137°), 8·4%; ortho- (by difference), 23%.

(Expt. 35.) Nitration yields, 95% (Found: C, 53·9; H, 5·1%). On oxidation the nitration mixture gave acids in 71% yield, which on separation gave: para-, m. p. 236° (alone or mixed), 68%; meta-, m. p. 126—128° (mixed m. p. 138—140°), 7·0%; ortho- (by difference), 25%.

Nitration of Methyl Benzylidenemalonate.—(Expt. 21.) The yield of mononitro-product was 96% (Found: C, 53·9; H, 4·2. Calc.: C, 54·3; H, 4·2%). The whole product was oxidised with 2%

potassium permanganate and gave nitrobenzoic acids in 93% yield (*M*, by titration, 164), the bulk of the *p*-nitrobenzoic acid being allowed to crystallise out in the pure state. Separation by the usual methods gave: para-, m. p. 235° (alone or mixed), 67%; impure meta-, m. p. 104—110°, 5·8%. The meta-acid was recrystallised from a small quantity of ethyl acetate–ligroin, and a quantity corresponding to 2·4%, m. p. 122—126° (mixed m. p. 133—138°) was obtained. Hence the composition of the nitration mixture is: para-, 67%; meta-, 2·4%; ortho- (by difference), 30·6%.

A second portion of the nitration product was crystallised from absolute alcohol before oxidation, and 61% of pure methyl *p*-nitrobenzylidenemalonate, m. p. 134° (either alone or mixed with a synthetic specimen), separated out. The residue from the mother-liquor on oxidation gave nitrobenzoic acids in 96% yield (*M*, by titration, 168·5), which on separation gave a further 5·2% of *p*- and 5·3% of *m*-nitrobenzoic acid, m. p. 113—120° (both calculated on whole nitration product); the latter on recrystallisation from ethyl acetate–ligroin gave 3%, m. p. 134—136° (mixed m. p. 137—139°). Hence the composition of the nitration product was: para-, 66·6%; meta-, 3%; ortho- (by difference), 30·8%.

(Expt. 22.) The yield of mononitration product was 96% (Found: C, 54·0; H, 4·2%), which on oxidation gave nitrobenzoic acids in 84% yield (*M*, by titration, 166); these on separation gave: para-, m. p. 238°, 67·8%; meta- (after crystallisation), m. p. 134—136°, 3·3%; ortho- (by difference), 28·9%. A second portion of the nitration product was crystallised from alcohol, and 65·4% of nearly pure methyl *p*-nitrobenzylidenemalonate separated, m. p. 133—134° (mixed m. p. with a synthetic specimen, 135—136°). The residue on oxidation gave nitrobenzoic acids in 82% yield, which on separation yielded a further 2% of para-, m. p. 220—223°, and 3% of meta- (after crystallisation), m. p. 133—135° (mixed m. p. 137—139°) (both calculated on the whole nitration product). Hence the composition of the nitration product is: para-, 67·4%; meta-, 3·0%; ortho- (by difference), 29·6%.

Nitration of Methyl Atropate.—(Expt. 41.) The yield of mononitro-products was theoretical (Found: C, 57·4; H, 4·5. Calc. for $C_{10}H_9O_4N$: C, 57·9; H, 4·4%), and crystallisation from absolute methyl alcohol gave 16·3% of pure *methyl* p-*nitroatropate*, m. p. 110° (unchanged by further crystallisation). The residue from the mother-liquor on oxidation gave nitrobenzoic acids in 85% yield (*M*, 173; benzoic acid, by sublimation, 3%), which on separation were found to contain 44% of *p*-nitrobenzoic acid, m. p. 220° (mixed m. p. 221—225°), and 9% of *m*-nitrobenzoic acid. The latter, however,

was slightly sticky, and was therefore converted into its methyl ester through the acid chloride, and the residue washed with a drop of methyl alcohol on porous porcelain; the residual ester had m. p. 75—78° (mixed m. p. 78°, with a synthetic specimen of methyl *m*-nitrobenzoate). Hence the composition of the nitration product is: para-, 16·3% + (44% of 83·7%) = 53%; meta-, approx. 9% of 83·7% = approx. 7%; ortho- (by difference), 40%.

(Expt. 42.) The yield of mononitro-product was 99% (Found: C, 57·4; H, 4·7%), which was completely oxidised to the mixed nitrobenzoic acids. These, on separation, gave para-, m. p. 220—222° (alone or mixed with a genuine specimen), 57%; meta-, m. p. 110—115° (mixed m. p. 133—135°), 4·7%; ortho- (by difference), 39·3%.

Nitration of Methyl Cinnamylidenemalonate.—In a preliminary experiment, the nitration product, on being poured on ice, gave a yellow, flocculent solid, which became sticky on filtering, and on drying overnight in a vacuum desiccator over phosphoric oxide decomposed to a semi-solid gum. The whole product was therefore oxidised with potassium permanganate, but gave only a 69% yield of mixed nitrobenzoic acids. On separation, this was shown to contain less than 2% of the meta-derivative. Under the following conditions, however, it was found possible to isolate the solid nitration product.

(Expt. 12.) The nitration was carried out with nitric acid (*d* 1·46), and the product was poured on ice, *partially* neutralised with a 10% solution of sodium hydroxide, and the separated solid rapidly filtered through a Buchner funnel surrounded with ice. After being washed with ice-cold water, the solid was quickly transferred to a vacuum desiccator over phosphoric oxide, and when dry was found to be quite stable. The aqueous mother-liquor and washings were extracted with ether, the ether extract washed five times with 2*N*-sodium carbonate solution, dried over calcium chloride, and the ether evaporated at the ordinary temperature. The yield of mono-nitration product was 103% (slight dinitration) (Found: C, 56·6; H, 4·5. Calc. for $C_{14}H_{13}O_6N$: C, 57·7; H, 4·5%). After two recrystallisations from methyl alcohol, 33·3% of practically pure methyl *p*-nitrocinnamylidenemalonate, m. p. 139—143°, separated, which after crystallisation from ethyl acetate–ligroin had m. p. 146°, either alone or mixed with a synthetic specimen. The residue from the combined mother-liquors was oxidised with a boiling 2% solution of potassium permanganate, and gave nitrobenzoic acids in 78% yield (*M*, by titration, 165). On separation, this fraction gave 9·5% of *p*-nitrobenzoic acid, whilst the meta-isomeride present was less than 1·5%, since only a negligible quantity

of the meta-barium salt crystallised out, the amount present, therefore, only being represented by the solubility correction. The composition of the nitration product was thus: para-, 33·3% + (9·5% of 66·6%) = 40% ; meta-, <1%; ortho- (by difference), 59%.

Summary.

Substance nitrated.	Proportion of isomerides present, *o*-.	*m*-.	*p*-.	Mean % of *m*-.	*p*-.
$CH_2Ph{\cdot}CH(CO_2Me)_2$	22·1	7·5	70·4		
	21·9	6·8	71·3		
	27·0	9·0	64·0	8	68
	23·0	8·4	68·6		
	25·0	7·0	68·0		
$CHPh{:}C(CO_2Me)_2$	30·6	2·4	67		
	30·8	3·0	66·2	3	67
	28·9	3·3	67·8		
	29·6	3·0	67·4		
$CPh(CO_2Me){:}CH_2$	40	approx. 7	53		
	39·3	4·7	57	5	55
$CHPh{:}CH{\cdot}CH{:}C(CO_2Me)_2$	59	<1	40	<1	40

The authors desire to express their thanks to Professor C. K. Ingold, F.R.S., for his interest and advice during the progress of this investigation, and to the Royal Society for defraying part of the expense incurred.

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CCLXXXIII.—1-*Phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic Acid.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM GERALD HUMPHREY.

ALTHOUGH it is well established that under the influence of acids, diketosuccinic acid phenylosazone is converted into 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone (I), the reduction of this compound to 1-*phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic acid* (II) has never been satisfactorily effected (compare Bernthsen, *Chem.-Ztg.*, 1898, 457; Eibner and Laue, *Ber.*, 1906, **39**, 2022). If, however, reduction is effected by using the theoretical amount of sodium amalgam, and the amino-acid is liberated in the presence of some excess of sulphur dioxide (to prevent oxidation), it can be isolated in a pure condition.

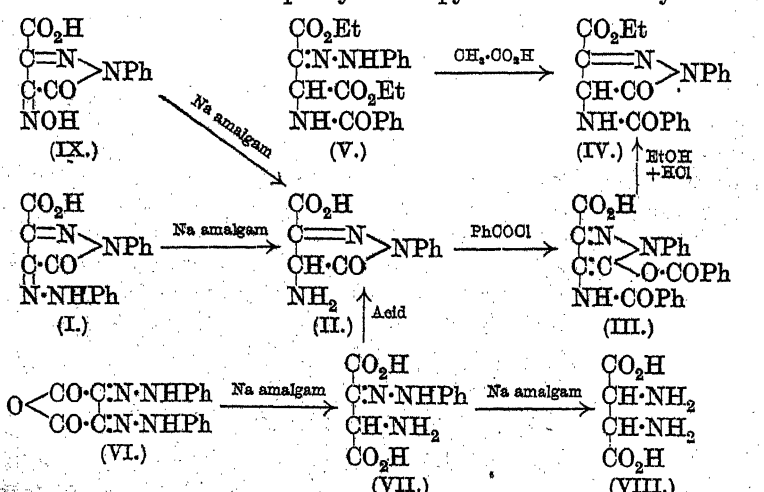
1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid is a white, crystalline solid of neutral reaction. It is very sparingly soluble in all ordinary organic solvents, but dissolves readily both in aqueous acids and in alkalis, such solutions oxidising rapidly in presence of

air, especially when warm. Alkaline solutions are the more readily oxidised, giving a silver mirror with ammoniacal silver oxide, and precipitating cuprous oxide from warm Fehling's solution. Acid solutions reduce ferric chloride and potassium permanganate in the cold.

It combines with 1 mol. of hydrogen chloride yielding a comparatively stable *hydrochloride*, which, however, turns violet on exposure to air. With acetic anhydride it gives a soluble, well-crystallised *acetyl* derivative of marked acid character. With benzoyl chloride it yields a *dibenzoyl* derivative, and on boiling this for a short time with alcohol containing a little hydrogen chloride, it is converted into ethyl benzoate and the ester of a monobenzoyl derivative (IV), identical with the compound obtained by Wislicenus by boiling ethyl oxalylhippurate phenylhydrazone (V) with acetic acid (*Ber.*, 1891, 24, 1260).

1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid may be obtained in several other ways. For example, it is formed when the alkaline solution of amino-oxalacetic acid phenylhydrazone (VII), obtained by partial reduction of anhydrodiketosuccinic acid phenylosazone (VI) by sodium amalgam, is acidified, ring closure occurring under the influence of acids, just as in the case of diketosuccinic acid phenylosazone.

The amino-ketopyrazoline has also been prepared by reduction of the corresponding oximino-compound (IX), obtained by the action of nitrous acid on 1-phenyl-5-ketopyrazoline-3-carboxylic acid.



The action of bromine upon 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone has been re-examined and

the product shown to be 1-*phenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-p-*bromophenylhydrazone*, since on reduction it yields *p*-bromoaniline and 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid. This constitution has been confirmed by its synthesis from 1-phenyl-5-ketopyrazoline-3-carboxylic acid and *p*-bromobenzenediazonium chloride.

Anhydrodiketosuccinic acid phenylosazone, like the corresponding halogenated derivatives (Chattaway and Humphrey, this vol., p. 1327), reacts with alcohols containing hydrogen chloride to give esters of the isomeric pyrazoline derivative. Several of these esters have been prepared, and it is noteworthy that the n-*propyl* and n-*butyl* esters have almost the same melting points.

EXPERIMENTAL.

Reduction of 1-*Phenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic Acid* 4-*Phenylhydrazone* (I) *to* 1-*Phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic Acid* (II).—17 G. of the phenylhydrazone were dissolved in 500 c.c. of a hot 1% solution of sodium hydroxide and placed in a wide-necked bottle closed by a cork, through which passed a wide glass tube reaching to the surface of the liquid and loosely stoppered at its upper end. The bottle was placed in a freezing mixture until about half of the liquid had frozen, and the air above the liquid was displaced by loosening the cork and passing a rapid stream of hydrogen down the tube. Successive small quantities of 2½% sodium amalgam were then introduced down the tube, and the mixture was vigorously shaken after each addition until the solution just became colourless and turbid due to the separation of aniline; about 250 g. of amalgam were required, and the reduction occupied 2—3 hours. The mixture was poured immediately into 800 c.c. of 2½% sulphuric acid (saturated with sulphur dioxide) and cooled to 0°. The 1-*phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic acid* at once separated as a white, crystalline precipitate. It was filtered off immediately, washed thoroughly with air-free water, alcohol, and ether, and dried in a vacuum desiccator over calcium chloride; yield, 10 g.; m. p. 225° (decomp.; with darkening from 215°) (Found: C, 54·6; H, 3·9; N, 18·8. $C_{10}H_9O_3N_3$ requires C, 54·8; H, 4·1; N, 19·2%). This acid is comparatively stable when dry, but slowly oxidises and turns brownish-pink on keeping. It is very sparingly soluble in water or ether, and only sparingly soluble in boiling alcohol, benzene, chloroform, or acetone; such solutions rapidly oxidise and turn brown on exposure to air; it was therefore impossible to purify the compound by crystallisation.

The *hydrochloride* separates on cooling a hot saturated solution of the amino-ketopyrazoline in concentrated hydrochloric acid.

It forms long, colourless prisms which begin to darken and decompose at 160°; it is fairly stable when dry, but its aqueous solution darkens on keeping and the crystals themselves slowly become pale violet (Found: C, 13·7. $C_{10}H_{10}O_3N_3Cl$ requires Cl, 13·9%).

Acetyl derivative. 1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid dissolves apparently unchanged in boiling acetic anhydride, the solution rapidly turning dark reddish-brown owing to oxidation. On adding a drop of concentrated sulphuric acid, a vigorous reaction occurs; on adding a few drops of water and cooling, the *acetyl* compound crystallises out. It is easily soluble in hot acetic acid, from which it separates in long, colourless prisms, m. p. 216° (Found: C, 55·0; H, 4·2; N, 16·0. $C_{12}H_{11}O_4N_3$ requires C, 55·2; H, 4·2; N, 16·1%).

Dibenzoyl derivative (III). When an alkaline solution of 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid is shaken with excess of benzoyl chloride, it is converted into a *dibenzoyl* derivative. The same compound is more readily prepared by heating the amine (2 g.) with benzoyl chloride (3 c.c.) until hydrochloric acid is no longer evolved, cooling, and adding ether. It was recrystallised from boiling acetic acid, in which it is easily soluble and from which it separates in long, colourless prisms, m. p. 205° (Found: C, 67·7; H, 3·9; N, 10·0. $C_{24}H_{17}O_5N_3$ requires C, 67·5; H, 4·0; N, 9·8%).

Ethyl ester of 1-phenyl-4-benzamido-5-ketopyrazoline-3-carboxylic acid (IV). When the dibenzoyl derivative (III) is boiled for a short time with alcohol containing 1% of hydrogen chloride, an ethyl group is introduced and one benzoyl group removed. The bright yellow solution thus obtained smells strongly of ethyl benzoate, and on cooling, the *ethyl* ester separates in long, slender, canary-yellow prisms, m. p. 195° (Found: N, 12·1. $C_{19}H_{17}O_4N_3$ requires N, 12·0%).

Preparation of 1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic Acid by Reduction of Anhydrodiketosuccinic Acid Phenylosazone.—The reduction of anhydrodiketosuccinic acid phenylosazone proceeds in two stages. The reduction by alkaline reducing agents of one phenylhydrazone group must first give amino-oxalacetic acid phenylhydrazone; this, however, cannot be isolated, for on acidification ring closure and pyrazoline formation occur and 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid is produced. This change was to be expected, since the disodium salt of the osazone is itself converted quantitatively into a pyrazoline derivative on acidification.

The reduction of both phenylhydrazone groups by alkaline reducing agents yields the two stereoisomeric diaminosuccinic acids, which separate when the solution is acidified. These compounds

were prepared by Farchy and Tafel by reduction of the osazone (*Ber.*, 1893, **26**, 1980).

Partial reduction. A fine suspension of 17 g. of anhydrodiketosuccinic acid phenylosazone in 500 c.c. of 1% sodium hydroxide solution was cooled in a freezing-mixture and treated with successive small quantities of 2½% sodium amalgam in the apparatus described above, until the yellow colour had just disappeared; about 250 g. of the amalgam were required. The colourless liquid was then decanted from the remaining mercury and slowly poured into 800 c.c. of ice-cold 2½% sulphuric acid saturated with sulphur dioxide; 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid then separated as a white precipitate which was filtered off, washed, and dried as before; yield, 9 g. It was shown to be identical with the compound previously described, since it melted at 215—225° with complete decomposition, and yielded an identical acetyl derivative, m. p. 216°.

Complete reduction. A fine suspension of 19 g. of the anhydride in 500 c.c. of a 1% aqueous solution of sodium hydroxide was cooled and reduced with a considerable excess of 2½% sodium amalgam (650 g.) in the manner described by Farchy and Tafel for the corresponding osazone. From the alkaline solution thus obtained, the two stereoisomeric diaminosuccinic acids were isolated and purified in precisely the same manner as described by Farchy and Tafel. The two isomerides were identified by conversion to their dibenzoyl derivatives; the dibenzoyl derivative of the *meso*-modification melts with decomp. at 213°, and that of the *r*-acid at 183°.

1-*Phenyl*-4-*oximino*-5-*ketopyrazoline*-3-*carboxylic Acid* (IX).—10 G. of 1-phenyl-5-ketopyrazoline-3-carboxylic acid (prepared from ethyl oxalacetate phenylhydrazone, as described by Wislicenus, *Annalen*, 1888, **246**, 319) and 5 g. of sodium nitrite were dissolved in 150 c.c. of 30% aqueous potassium hydroxide; the solution was cooled to 0° and added slowly to 200 c.c. of 10% hydrochloric acid. The *oximino*-compound separated as a red precipitate, which after 12 hours was filtered off and crystallised from acetic acid, in which it is easily soluble, and from which it separates in glittering, red, slender prisms, m. p. 209° (decomp.); yield, 9 g. (Found: N, 17·8. $C_{10}H_7O_4N_3$ requires N, 18·0%).

When reduced it yields 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid. A solution of 2 g. of the oximino-compound in 100 c.c. of a 1% aqueous solution of sodium hydroxide was cooled in a freezing mixture and reduced with 40 g. of 2½% sodium amalgam. The colourless solution was then poured into 120 c.c. of 3% sulphuric acid, saturated with sulphur dioxide. The amino-keto-

pyrazoline separated as a white, crystalline powder, which was filtered off, washed, and dried as before. Yield 1·7 g. It was identified by its acetyl derivative, m. p. 216°.

Bromination of 1-Phenyl-4 : 5-diketopyrazoline-3-carboxylic Acid 4-Phenylhydrazone.—In view of recent work on the bromination of phenylhydrazones (J., 1925, 127, 975, 1687, 2407; this vol., p. 1323), it was of interest to determine to what extent bromine would enter the phenylhydrazone residue in 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone. 6 G. (1 mol.) of the hydrazone were suspended in 400 c.c. of glacial acetic acid containing 4 c.c. (4 mols.) of bromine, and boiled for 8 hours. Hydrogen bromide was evolved, and on cooling, the *bromination product* separated as a yellow solid. It was crystallised from boiling acetic acid, in which it is sparingly soluble, and from which it separates in short, yellow prisms, m. p. 258° (decomp.). Yield, 6 g. (Found : Br, 20·6. $C_{16}H_{11}O_3N_4Br$ requires Br, 20·7%).

The bromine was shown to have entered the para-position by the production of *p*-bromoaniline on reduction : 5 G. of the bromination product were dissolved in 150 c.c. of 1% aqueous sodium hydroxide and reduced as before with 80 g. of 2½% sodium amalgam; when this was poured into 200 c.c. of 2½% sulphuric acid, saturated with sulphur dioxide, 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid separated as a white precipitate (yield, 2 g.; acetyl derivative, m. p. 216°). The acid filtrate was concentrated, made alkaline with caustic soda and steam-distilled. *p*-Bromoaniline (m. p. 63°) distilled over, and was identified by conversion to its acetyl derivative, m. p. 167°.

The constitution of the bromination product was further established by its synthesis from 1-phenyl-5-ketopyrazoline-3-carboxylic acid by the action of *p*-bromobenzenediazonium chloride. 2 G. of *p*-bromoaniline were suspended in 3·5 c.c. of concentrated hydrochloric acid and diazotised with 1 g. of sodium nitrite in 25 c.c. of water; the small excess of nitrous acid was removed by bubbling air through the solution, which was then added to a solution of 2 g. of 1-phenyl-5-ketopyrazoline-3-carboxylic acid in 100 c.c. of a 2% aqueous solution of potassium hydroxide. 1-Phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-*p*-bromophenylhydrazone separated as a yellow precipitate, which, after the addition of excess of hydrochloric acid, was filtered off, washed with hot alcohol, and crystallised from acetic acid. It melted at 258° (decomp.) and was identical in all respects with the compound obtained by the direct bromination (above).

In the course of this investigation, several esters of 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone have

been prepared by the action of alcohols containing hydrogen chloride on anhydrodiketosuccinic acid phenylosazone. The *methyl* ester, obtained by boiling the phenylosazone (2 g.) for 24 hours with methyl alcohol (30 g.) saturated with dry hydrogen chloride, crystallises from alcohol, in which it is easily soluble, in fine, yellow needles, m. p. 138° (Found: N, 17·4. $C_{17}H_{14}O_3N_4$ requires N, 17·4%). The ethyl ester (Wislicenus and Scheidt, *Ber.*, 1891, **24**, 4210), m. p. 153°, is obtained in a similar manner. The n-*propyl* ester crystallises from acetic acid, in which it is easily soluble, in long, deep yellow prisms, m. p. 116·5° (Found: C, 65·0; H, 4·9; N, 16·1. $C_{19}H_{18}O_3N_4$ requires C, 65·1; H, 5·1; N, 16·0%). The n-*butyl* ester crystallises from acetic acid in long prisms, not quite so deep in colour as those of the *n*-propyl ester but melting at practically the same temperature, 117° (a mixture of these two esters had m. p. 112°) (Found: C, 66·2; H, 5·5; N, 15·5. $C_{20}H_{20}O_3N_4$ requires C, 65·9; H, 5·5; N, 15·4%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, June 29th*, 1927.]

CCLXXXIV.—*The Action of Hydrogen Iodide on Nitroso-compounds.*

By JOHN CAMPBELL EARL and JAMES KENNER.

THE observation of the ortho-para directive influence of the nitroso-group in aromatic substitution was considered by Ingold (J., 1925, **127**, 513) to be in conflict with the theory of induced alternate polarity, but a theoretical discussion of the nitroso-group by Robinson (*Chem. and Industry*, 1925, **44**, 456) showed this to be at least not necessarily the case. In addition, it was pointed out (Kenner, Tod, and Witham, J., 1925, **127**, 2343) that, quite apart from any purely theoretical considerations, the well-known liberation of iodine from hydrogen iodide by nitrous acid, by hypochlorous acid, and by hydrogen peroxide is a simple experimental indication of possible similarity in polar properties of the nitroso-group, the chlorine atom, and the hydroxyl group. The analogy is not perfect, since in the case of nitrous acid the primary nitrogenous product undergoes a further reaction with formation of nitric oxide, but a parallelism also exists between the behaviours of the nitroso-group and chlorine, in that each is readily displaced from *N*-nitroso- or -chloro-amines and -acetanilides (von Pechmann and Frobenius, *Ber.*, 1894, **27**, 651).

It seemed that further evidence in regard to the nature of the nitroso-group might be obtained from a study of the action of

hydrogen iodide on nitroso-compounds in general. Reference to the literature showed that among aliphatic compounds, iodine is liberated from hydrogen iodide by the nitrosochlorides of tetramethylethylene (I) (Thiele, *Ber.*, 1894, **27**, 456) and $\Delta^{4(8)}$-menthen-1-ol (γ-terpineol) acetate (II) (Baeyer, *ibid.*, p. 446). Later, Baeyer showed the

(I.) $Me_2C(NO)\cdot CMe_2Cl$ $\qquad$ $Me_2C(NO)\cdot C(Cl)<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}Me\\OAc\end{matrix}$ (II.)

$Me_2C(NH\cdot OH)\cdot C(Br)<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}Me\\Br\end{matrix}$ (III.)

nitrosobromide of 1-bromo-$\Delta^{4(8)}$-menthene to be converted into the hydroxylamino-derivative (III) by hydrogen bromide, in the presence of red phosphorus as an absorbent of the bromine liberated, and concluded that the reaction with hydrogen iodide follows a similar course. Baeyer observed (*loc. cit.*) that the nitrosochlorides of tetramethylethylene and menthenol acetate behaved differently towards hydrogen bromide in acetic acid. There is, however, no essential difference between the two reactions. The product derived from tetramethylethylene nitrosochloride is a basic substance, which, like the compounds examined by Baeyer, loses the elements of hydrogen chloride when it is liberated in the presence of alkali. The colourless *hydrochloride* of the resulting unsaturated base exhibits reducing properties and its composition corresponds with the formula (IV). In further support of the constitution

$Me_2CCl\cdot Me_2C\cdot NO \longrightarrow Me_2CCl\cdot Me_2C\cdot NH\cdot OH \longrightarrow MeC{:}CH_2\cdot Me_2C\cdot NH\cdot OH,HCl$ (IV.)

assigned to this compound, it was shown to furnish a *condensation product* with salicylic aldehyde, the composition of which was in accord with the formula (V) (compare Bamberger, *Ber.*, 1894, **27**, 2556).

(V.)

There seemed also a possibility that the negative character of the nitroso-group might induce positive polarity in the chlorine atom, which, in the presence of hydrogen iodide, would render it liable to displacement by hydrogen. It was, however, shown that this does not occur in either of the above instances, since the quantity of iodine liberated in the reaction was found to correspond approximately with the decrease in the amount of halogen ion present in solution. The slight discrepancy was shown to be attributable to formation of chlorine ions by hydrolytic action, which

occurred in absence of hydrogen iodide under otherwise similar experimental conditions.

Since the conditions for the transmission of the influence of the nitroso-group to the chlorine atom should be more favourable in the aromatic nucleus than in the above compounds, the behaviour of *p*-chloronitrosobenzene towards hydrogen iodide was investigated. Here also reduction occurred, being immediately followed by condensation of the hydroxylamine with the nitroso-derivative, so that 4 : 4′-dichloroazoxybenzene was produced in excellent yield. No elimination of halogen occurred from *p*-chloronitrosobenzene or from its meta-isomeride under the conditions employed. The nitroso-group itself is therefore the sole point of attack by hydrogen iodide in such cases. Doubtless its reactivity in the aromatic compounds is affected by the position of the chlorine atom, but our hopes of demonstrating this relationship could not be realised owing to the uncertainty as to the relative proportions of polymerised and unpolymerised material present in solution, and to the condensation of nitroso- with hydroxylamino-derivatives just mentioned.

In order further to demonstrate the general character of the reaction here discussed, δ-nitroso-δ-methylpentan-β-one (VI) (Harries, *Ber.*, 1898, **31**, 1379), 8-nitrosomenthone (VII) (Harries and Rolder, *Ber.*, 1899, **32**, 3365), and 4-nitrosomenthone (VIII) (Baeyer, *Ber.*, 1894, **27**, 1912; 1895, **28**, 1586) were examined qualitatively in respect of their behaviour towards hydrogen iodide.

(VI.) $CMe_2(NO)\cdot CH_2\cdot COMe$ $\quad$ $Me_2C(NO)\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}>CHMe$ (VII.)

$Me_2CH\cdot C(NO)<\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}>CHMe$ (VIII.)

In each case, iodine was liberated, but the rate of reaction, as in other cases, was affected by the degree of polymerisation of the nitroso-compounds.

It may therefore be concluded that nitroso-compounds, in general, are reduced by hydrogen iodide to the corresponding hydroxylamines. The facility with which this occurs is in remarkable contrast to the behaviour of carbonyl compounds, with which nitroso-compounds are in some respects comparable. The significance of this contrast will be dealt with in a subsequent paper discussing the chemistry of nitroso-compounds. Meanwhile, the possibility must be entertained in the case of nitrous acid, also, that

$$HO\cdot NO \longrightarrow HO\cdot NH\cdot OH \text{ (IX.)} \qquad H\cdot NO \text{ (X.)}$$

the primary action leads to the formation of dihydroxyammonia (IX) rather than of nitroxyl (X), as might be anticipated from the

analogy between the nitroso- and hydroxyl groups or the chlorine atom mentioned at the outset of this paper. This possibility must also be regarded as the more probable, when it is recalled that the ultimate nitrogenous product of the reaction is nitric oxide, the formation of which could be represented by the equation $NH(OH)_2 + HO{\cdot}NO \longrightarrow 2NO + 2H_2O$ (compare Raschig, "Schwefel und Stickstoffstudien," Leipzig, 1925, p. 19; Angeli and Angelico, *Gazzetta*, 1900, **30**, i, 593; *Ber.*, 1904, **37**, 2390).

EXPERIMENTAL.

Reduction of Tetramethylethylene Nitrosochloride by Hydrogen Bromide.—A concentrated glacial acetic acid solution of hydrogen bromide (42 c.c.) was mixed with red phosphorus (1·4 g.) and cooled in ice-water until crystallisation commenced (12°); tetramethylethylene nitrosochloride (7 g.) was then added with thorough stirring. The reaction was completed by passing a stream of hydrogen bromide into the ice-cooled mixture during a period of 1 hour, and stirring for another 2 hours. The liquid was then added to a mixture of ice (60 g.) and water (60 g.), and the undissolved material filtered off. Benzene (50 c.c.) was added, together with sufficient sodium hydroxide solution to render the aqueous layer strongly alkaline. The liberated base passed into solution in the benzene, and after further extraction of the alkaline solution with benzene, the united extracts were shaken four times with hydrochloric acid (25 c.c.) diluted with an equal volume of water. The solid residue obtained by evaporating the united acid extracts to dryness under reduced pressure was purified by filtering its solution in alcohol, and again evaporating to dryness. The *hydrochloride* of *β-hydroxyl-amino-βγ-dimethyl-Δ$^{\gamma}$-butene* so obtained (4·5 g.) was further purified by recrystallisation from alcohol (Found: N, 9·5; Cl, 23·1. $C_6H_{13}ON,HCl$ requires N, 9·2; Cl, 23·2%). The base reduced Fehling's solution in the cold.

When the hydrochloride (0·8 g.) was dissolved in water (5 c.c.) with the addition of crystalline sodium acetate (1·2 g.), salicylic aldehyde (0·65 g.), and alcohol (5 c.c.), condensation readily occurred at the ordinary temperature. After 19 hours, the mixture was poured into ice water, and an oil separated which soon crystallised. The solid (0·55 g.) was filtered off, and a further quantity (0·2 g.) separated on saturating the filtrate with salt and cooling in ice. After one crystallisation from alcohol, the *condensation product* melted sharply at 53° (Found, by micro-analysis: N, 6·4. $C_{13}H_{17}O_2N$ requires N, 6·4%).

Reduction of Tetramethylethylene Nitrosochloride by Hydrogen Iodide.—A solution of the nitrosochloride (0·1355 g.) in pure benzene

(10 c.c.) was shaken with a mixture of an approximately $N/5$-solution of potassium iodide (corresponding to 19·94 c.c. of accurately $N/5$-solution) and an approximately $N/2$-solution of sulphuric acid (20 c.c.). After 3½ hours, the benzene layer, which contained the bulk of the liberated iodine, was separated, and the aqueous layer extracted with benzene until practically colourless. The halogen ion in the aqueous solution was then titrated with silver nitrate and potassium thiocyanate in the usual way, and found equivalent to 13·12 c.c. of $N/5$-solution. The united benzene solutions were shaken with excess of standard sodium thiosulphate, the excess being titrated with standard iodine. The iodine thus determined corresponded to 7·43 c.c. of $N/5$-solution.

It would thus appear that halogen corresponding to 0·61 c.c. of $N/5$-solution had been furnished by elimination of chlorine from the nitrosochloride. This occurred by hydrolysis, for when a similar benzene solution of the nitrosochloride was shaken for 3½ hours with dilute sulphuric acid under very similar conditions, the aqueous layer contained halogen corresponding to 2·0 c.c. of $N/5$-solution. In this case, of course, there was no decrease in the concentration of the nitrosochloride solution owing to reduction during the experiment, so that the amount of hydrolysis is higher than in the reduction experiments.

Reduction of γ-Terpinyl Acetate Nitrosochloride by Hydrogen Iodide.—The reaction was slower than in the case of the tetramethylethylene derivative so that a higher concentration of the nitrosochloride (0·2466 g. in 10 c.c. of benzene) was employed, and the shaking was continued for 5 hours. In other respects, the experimental conditions were similar to those described above.

Halogen originally present in aqueous solution = 19·94 c.c.
" finally " " " " = 18·75 c.c.
Iodine liberated = 1·37 c.c.

Here, again, there is evidence of slight hydrolysis.

Reduction of Chloronitrosobenzenes by Hydrogen Iodide.—Both the *m*- and *p*-isomerides were examined in the usual way, 0·5 g. of the substance in benzene (10 c.c.) being used, and the shaking being continued for 4 hours.

	m-.	*p*-.
Halogen originally present in aqueous solution (c.c. of $N/5$)	19·94	19·94
" finally " " " "	17·82	18·72
Iodine liberated (c.c. of $N/5$)	2·08	1·57

These results indicate a similarity in behaviour to the two nitrosochlorides, but in neither case was there any evidence of the removal of chlorine by hydrolysis.

An attempt was made to modify the reduction in such a way that

the isolation of the reduction products would be possible. For this purpose, it was necessary to introduce some substance to remove the iodine as formed. Red phosphorus, mercury, and sodium thiosulphate were all successfully employed. Thus a mixture of *p*-chloronitrosobenzene (1 g.) red phosphorus (1 g.), and glacial acetic acid (25 c.c.) was well stirred at room temperature, and hydriodic acid (*d* 1·7; 5 c.c.) added drop by drop during 5 minutes. The mixture became warm and a mass of crystalline material separated. After a further 5 minutes, water was added, and the precipitated material was filtered off and washed thoroughly with water. The *pp'*-dichloroazoxybenzene was extracted from the residue by repeated maceration with ether, and the solvent allowed to evaporate at room temperature. The product so obtained (0·83 g.) melted at 153—154°, and at 154° after one recrystallisation from alcohol (Found, by micro-analysis: N, 10·7. Calc. for $C_{12}H_8ON_2Cl_2$: N, 10·5%). In another experiment the azoxy-compound (0·7 g., m. p. 153°) was obtained from the nitroso-derivative (0·85 g.), glacial acetic acid (25 c.c.), mercury (9·5 g.), and hydriodic acid (*d* 1·7; 3 c.c.).

From *m*-chloronitrosobenzene by means of phosphorus, *mm'*-dichloroazoxybenzene, m. p. 96°, was obtained (Found: N, 10·1%).

Action of Hydriodic Acid on the Nitroso-derivatives.—δ-Nitroso-δ-methylpentan-β-one yielded a colourless solution in acetone, which only reacted very slowly at the ordinary temperature with hydriodic acid, but when the solution was first warmed until a definite blue colour had developed, and then cooled, liberation of iodine occurred much more rapidly. 8-Nitrosomenthone, though blue when first prepared, slowly polymerises and therefore also reacts comparatively slowly with hydriodic acid in acetone solution. 4-Nitrosomenthone was definitely recognised by Baeyer (*loc. cit.*) to be a bis-compound, but nevertheless has some tendency towards dissociation since its solution in xylene became blue when heated. Although no similar development of colour occurred in boiling acetone solution, yet iodine was slowly liberated when a cold solution in acetone was treated with hydriodic acid.

Note on the Action of Hydriodic Acid on Ether.—Whilst it is well known that hydrogen iodide reacts with ethyl ether to form ethyl iodide, it is not recorded in the standard work of reference that they react in some way at the ordinary temperature with formation of iodine. This was observed in connexion with the experiments now described, and prevented the use of ether as solvent in cases where it would otherwise have been very desirable. The only reference to this reaction which we have been able to find is a statement by Hantzsch, who experienced the same difficulty and stated

that "Jodwasserstoff in diesem Medium schon durch unvermeidliche Spuren von Sauerstoff zum Trijodwasserstoff oxydiert wird" (*Z. Elektrochem.*, 1923, **29**, 232). In a quantitative experiment with ether purified in the usual manner (20 c.c.), aqueous potassium iodide solution (*N*/5, 20 c.c.), and dilute sulphuric acid (*N*/2, 20 c.c.), the iodine liberated after some days at the ordinary temperature required 8·5 c.c. of *N*/10-thiosulphate.

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CCLXXXV. — *Co-ordination Compounds of Quinquevalent Molybdenum.*

By ROBERT GILBERT JAMES and WILLIAM WARDLAW.

ONE important result of the application of electronic theories of valency to co-ordination compounds has been to indicate the relative stabilities of the systems within the co-ordination sphere. The marked stability of the ion $Mo(CN)_8''''$, present in an aqueous solution of the complex salt $K_4Mo(CN)_8$, can be readily appreciated when it is seen that the effective atomic number of the molybdenum is 54—that of the next inert gas—and that the associating units are regularly distributed. The stability of complex salts is not, however, the same for all associated units, the order of decreasing stability being cyanides, fluorides, thiocyanates, chlorides, bromides, and iodides, and this third factor must always have consideration. In a recent investigation (this vol., p. 512) on the complex chlorides of tervalent molybdenum, such as K_3MoCl_6 and K_2MoCl_5,H_2O, it was shown that ionisation in dilute aqueous solution produced initially four and three ions, respectively, but that the complex ions were gradually decomposed. Here, the effective atomic number of the metallic atom is 51 and the decreased stability of the complex ion $MoCl_6'''$, compared with that of the ion $Mo(CN)_8''''$, is due primarily to the smaller number of electrons associated with the molybdenum atom, but also to the replacement of the cyanide by the chloride radical. With the chlorides of quinquevalent molybdenum of the general formula $R_2[MoOCl_5]$, the effective atomic number of the central atom has fallen to 49, and this is reflected in the marked changes which occur when these green, crystalline substances are dissolved in water. They give, immediately, brown solutions with acid reactions, from which it is impossible to obtain the original salt satisfactorily by crystallisation. Although these facts are well known, no systematic examination of this decomposition has hitherto been attempted. In the present research,

this has been done, and not only has it yielded information as to the course of the reaction in aqueous solution, but it has resulted in the evolution of improved methods of preparation for the complex salts themselves, and in the isolation of new series of co-ordination compounds characteristic of the intermediate stages of the hydrolytic decomposition.

EXPERIMENTAL.

Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173) first showed that by electrolytic reduction of molybdenum trioxide, dissolved in hydrochloric acid of appropriate concentration, a solution containing quinquevalent molybdenum could be obtained if a platinised platinum cathode was used, whereas with a cathode of polished platinum, reduction to the tervalent state resulted. This observation has been utilised in the following preparations.

Molybdenum trioxide solution. Molybdenum trioxide (100 g.) was heated with 500 c.c. of hydrochloric acid (*d* 1·16) till dissolved; the solution was evaporated to 250 c.c., filtered, and made up to 500 c.c. with hydrochloric acid, and thus contained molybdenum trioxide (20%) in 9*N*-hydrochloric acid.

Salts of the Type $R_2[MoOCl_5]$.

Diammonium Molybdenyl Pentachloride.—Klason (*Ber.*, 1901, **34**, 148) and Nordenskjold (*ibid.*, p. 1572) obtained this salt by reducing ammonium molybdate in concentrated hydrochloric acid with hydrogen iodide, whilst Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458), using Chilesotti's results (*loc. cit.*), prepared it by the electrolytic reduction method, of which the following is a variation: 75 C.c. of the molybdenum trioxide solution, diluted with an equal volume of water, were placed in the cathode chamber of a diaphragm cell, of which the anode chamber contained hydrochloric acid (5*N*). A polished platinum electrode served as the anode, whilst the cathode was of platinised platinum, 5 cm. square. A current of 2·5 amp. was employed, and on electrolytic reduction to the quinquevalent stage, a reddish-brown cathode solution was obtained. This was concentrated to 50 c.c. under diminished pressure, 30 c.c. of ammonium chloride solution (containing 9 g.) were admitted, and the mixture was heated for about a minute. On saturating with hydrogen chloride and cooling, emerald-green crystals separated. These were recrystallised by dissolving in the minimum volume of water at *ca.* 80°, and saturating with hydrogen chloride until cold. The crystals were washed with concentrated hydrochloric acid and dried in a vacuum over solid potassium hydroxide.

Analysis. The molybdenum was precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide, the chloride

in the filtrate and washings being estimated as silver chloride. The ammonia was determined by the distillation method, the ammoniacal distillate being titrated continuously against standard acid with bromophenol-blue as indicator [Found: Mo, 29·5; Cl, 54·4; NH_4, 11·1. Calc. for $(NH_4)_2MoOCl_5$: Mo, 29·5; Cl, 54·5; NH_4, 11·1%].

A New Electrolytic Method.—150 C.c. of the prepared molybdenum trioxide solution were placed in the cathode chamber of the diaphragm cell, the anode chamber containing ammonia (10*N*) and a small quantity of ammonium chloride. On electrolysis with a current density of 0·1 amp. per sq. cm. and continuous saturation of the cathode liquid with hydrogen chloride, the diammonium molybdenyl pentachloride separated in good yield. After being washed and dried, the crystals gave Mo, 29·3; Cl, 54·6; NH_4, 11·1%.

Dirubidium Molybdenyl Pentachloride.—This salt was first prepared by Nordenskjold (*loc. cit.*) and later by Foerster and Fricke (*loc. cit.*). By the use of the first of the methods here described for the preparation of the ammonium salt, but adding 30 c.c. of a rubidium chloride solution (containing 14 g.), yellowish-green crystals were obtained, which were washed, dried, and recrystallised (Found: Mo, 20·9; Cl, 38·6; Rb, 36·9. Calc. for Rb_2MoOCl_5: Mo, 20·9; Cl, 38·5; Rb, 37·1%).

Dipotassium Molybdenyl Pentachloride.—The methods described by Nordenskjold and by Foerster and Fricke for the preparation of this salt were found always to give a product contaminated with potassium chloride. The following method gave an excellent yield of pure salt, which, being crystallised at a high temperature, was obtained free from the more soluble alkali chloride: 75 C.c. of molybdenum trioxide solution, diluted with 75 c.c. of water, were electrolytically reduced to the quinquevalent condition. The resulting solution was concentrated under diminished pressure to 50 c.c., 30 c.c. of potassium chloride solution (containing 6·5 g.) were added, and the solution was further concentrated to 70 c.c. The flask was now placed in a thermostat at 90°, and the solution saturated with hydrogen chloride. With the hydrogen chloride still passing through the solution, the temperature was lowered to 70°, whereupon the required green salt began to separate; the temperature of the thermostat was then altered to and maintained at 60° and a high yield of the complex salt was thus obtained. The dark green crystals were filtered through a hot filter, drained in a current of dry hydrogen chloride, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide [Found: Mo, 25·8; Cl, 47·4; K, 20·9. Calc. for K_2MoOCl_5: Mo, 26·1; Cl, 48·

K, 21·3%; the presence of a small amount of water of crystallisation ($0{\cdot}25H_2O$) accounts for the slight difference].

Dipyridinium Molybdenyl Pentachloride.—The only method previously described for the preparation of this salt is that of Rosenheim and Koss (*Z. anorg. Chem.*, 1906, **49**, 148) and of Sand and Burger (*Ber.*, 1906, **39**, 1761), who obtained it by the action of hydrochloric acid on the complex compound $Mo(OH)_2(CNS)_3(C_5H_5N)_2$. The following method gave an almost theoretical yield of pure salt: 150 C.c. of the molybdenum trioxide solution, reduced electrolytically to the quinquevalent stage, were evaporated on a water-bath under diminished pressure almost to dryness; alcohol, saturated with hydrogen chloride, was now admitted, and after warming and agitation, the reddish-brown mass dissolved producing an emerald-green solution (100 c.c.). This was cooled to room temperature, saturated with hydrogen chloride, and filtered if necessary; one half of the filtrate was utilised for the preparation of the pyridinium salt, and the other half for the quinolinium derivative. By the addition of alcohol saturated with hydrogen chloride, the 50 c.c. of solution were made up to 100 c.c., and to this water-cooled solution pyridine was added, drop by drop, with constant stirring till no more green precipitate separated (excess of pyridine gives a red solution). This was filtered and dissolved in alcoholic hydrogen chloride (2 vols. of alcohol, saturated with hydrogen chloride at room temperature, and 1 vol. of absolute alcohol). On concentrating this solution, yellowish-green crystals separated; these were filtered, washed with alcohol saturated with hydrogen chloride, and dried over potassium hydroxide and phosphoric oxide in a vacuum [Found: Mo, 21·4; Cl, 39·6; N, 6·2; C, 26·8; H, 2·7. Calc. for $(C_5H_6N)_2MoOCl_5$: Mo, 21·4; Cl, 39·5; N, 6·2; C, 26·7; H, 2·7%].

Diquinolinium molybdenyl pentachloride was prepared by adding pure quinoline (18 g.) with constant stirring to the boiling molybdenum solution previously mentioned. On evaporation and crystallisation, a large amount of the required substance was obtained, which was recrystallised and dried as in the case of the pyridinium compound [Found: Mo, 16·9; Cl, 31·2; N, 5·0; C, 37·8; H, 3·3. $(C_9H_8N)_2MoOCl_5,H_2O$ requires Mo, 16·9; Cl, 31·3; N, 4·9; C, 38·1; H, 3·2%].

Ditrimethylammonium Molybdenyl Pentachloride.—Nordenskjold (*loc. cit.*) prepared this salt by employing hydrogen iodide as a reducing agent. Using the electrolytic reduction method under conditions to be described later, the present authors isolated the first chloride of the type $R[MoOCl_4,H_2O]$ as *mono*trimethylammonium molybdenyl tetrachloride, $NMe_3H[MoOCl_4,H_2O]$ (see below), and converted it into the ditrimethylammonium pentachloride by

dissolving it in alcoholic hydrogen chloride, evaporating to small bulk, saturating with hydrogen chloride, and allowing to crystallise. After recrystallisation, the light emerald-green crystals were washed with alcoholic hydrogen chloride and dried in a vacuum over solid potassium hydroxide and phosphoric oxide {Found: Mo, 23·5; Cl, 43·2; N, 6·9; C, 17·6; H, 5·1. Calc. for $[(CH_3)_3NH]_2MoOCl_5$: Mo, 23·5; Cl, 43·3; N, 6·8; C, 17·6; H, 4·9%}.

General Properties of the Complex Salts.—The salts described in this paper generally crystallise in the rhombic form and range in colour from dark green through shades of emerald-green to yellowish-green. The pyridinium salt exhibits a strong pleochroism and has a very high double refraction. When exposed to a moist atmosphere, these salts more or less rapidly turn reddish-brown, in which condition they are very susceptible to aërial oxidation, molybdenum blue being formed. The pyridinium and the ditrimethylammonium salts give a bright copper-red substance at one stage of these changes. The potassium and the substituted-ammonium salts are the most sensitive, and the quinolinium the least sensitive, to the action of moist air. All the complex salts are soluble in water, the concentrated solutions being reddish-brown, passing through orange to bright yellow on dilution. On saturation with hydrogen chloride, these aqueous solutions finally turn emerald-green and from sufficiently concentrated solutions the complex salts separate. Alcohol dissolves all these green salts, and from the solution of the alkali complex salts, alkali chlorides separate on heating. The pyridinium salt under these conditions yields a red precipitate which will be referred to in detail later. The addition of pyridine or quinoline to aqueous solutions of any of the complex salts gives a brown, insoluble precipitate.

Physico-chemical Measurements.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

The figures given on p. 2150 indicate that the complex salts $R_2[MoOCl_5]$ undergo extensive ionisation in aqueous solution, and instead of yielding the (theoretical) 3 ions, furnish 9 ions in the reddish-brown solutions of concentrations *ca.* 0·02—0·05 g.-mol. per litre, and 10—11 ions in the bright yellow solutions obtained by further dilution. Additional evidence for this ionisation in aqueous solution is afforded by determinations of molecular conductivity. Table II gives the value of μ at 0° for various dilutions v (as litres per mol.).

A satisfactory explanation of the high molecular conductivity and the exceptional osmotic factor is forthcoming if it be assumed

TABLE I.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
Diammonium molybdenyl pentachloride.			
1·675	0·0515	9·00	36·15
0·725	0·0223	9·03	36·02
0·278	0·0085	10·1	32·21
M for $(NH_4)_2MoOCl_5 = 325·3$.			
Dipotassium molybdenyl pentachloride.			
2·308	0·0628	8·89	41·34
0·765	0·0208	9·12	40·30
0·285	0·0077	10·1	36·39
M for $K_2MoOCl_5 = 367·5$.			
Dirubidium molybdenyl pentachloride.			
1·567	0·0340	8·88	51·82
0·853	0·0185	9·11	50·52
0·457	0·0099	9·42	48·85
M for $Rb_2MoOCl_5 = 460·2$.			
Dipyridinium molybdenyl pentachloride.			
1·640	0·0365	8·77	51·23
0·765	0·0170	9·00	49·92
0·417	0·0093	9·84	45·66
M for $(C_5H_6N)_2MoOCl_5 = 449·3$.			
Diquinolinium molybdenyl pentachloride.			
1·150	0·0203	9·01	62·96
0·558	0·0098	9·89	57·35
0·269	0·0047	10·45	54·30
M for $(C_9H_8N)_2MoOCl_5,H_2O = 567·3$.			

TABLE II.

	$(NH_4)_2MoOCl_5$.				Rb_2MoOCl_5.			
v	199·2	796·8	1593·6	3187·2	51·14	409·1	818·2	1636·4
μ	755·3	865·6	916·8	948	689	849	919	973
	K_2MoOCl_5.				$[(CH_3)_2NH]_2MoOCl_5$.			
v	36·54	292·3	584·6	1169·3	59·76	239·0	478·1	1912·3
μ	676·6	834·3	897·3	954	644	757	836	935
	$(C_5H_5N)_2MoOCl_5$.				$(C_9H_8N)_2MoOCl_5$.			
v	54·7	437·5	875	1751	152	1216	2432	
μ	659·1	842·6	914·7	959	693	870	929	

that the complex ion $MoOCl_5''$ is unstable, and that ionisation and hydrolysis occur in accordance with the following scheme:

$$\begin{aligned}
R_2[MoOCl_5] + H_2O &\rightleftharpoons R[MoOCl_4,H_2O] + RCl,\\
R[MoOCl_4,H_2O] + H_2O &\rightleftharpoons [MoOCl_3,2H_2O] + RCl,\\
[MoOCl_3,2H_2O] + H_2O &\rightleftharpoons [MoO(OH)Cl_2,2H_2O] + HCl,\\
[MoO(OH)Cl_2,2H_2O] + H_2O &\rightleftharpoons [MoO(OH)_2Cl,2H_2O] + HCl,\\
&\rightleftharpoons [MoO_2Cl,3H_2O] + HCl,\\
[MoO_2Cl,3H_2O] + H_2O &\rightleftharpoons [MoO_2(OH),3H_2O] + HCl,
\end{aligned}$$

Whence, at infinite dilution:

$$R_2[MoOCl_5] + 5H_2O \rightleftharpoons [MoO_2(OH),3H_2O] + 2RCl + 3HCl.$$

In the first place, it is seen from such a scheme of ionisation that 10 ions should result at infinite dilution and that the osmotic factor should be 11. These theoretical deductions are in accordance with the experimental data. The ionic velocities at 0° deduced from the values at 18° (Landolt–Börnstein, "Tabellen," 1923, ii, 1104) are: $H^{\cdot} = 227{\cdot}6$; $Cl' = 40{\cdot}0$; $Rb^{\cdot} = 41{\cdot}5$; $NH_4^{\cdot} = 38{\cdot}4$. From the ammonium and rubidium salts, for example, which on the proposed scheme of ionisation should each yield at infinite dilution 2 metal (or ammonium), 3 hydrogen, and 5 chlorine ions, a molecular conductivity of 959·6 and 965·8, respectively, would be expected. Since, for the pyridinium ion an ionic velocity of 20 is obtained at 0° (Landin, *J. Chim. physique*, 1907, **5**, 592), the value of μ_∞ for the pyridinium complex salt should be 923. Reference to the experimental values shows that they are in good agreement with these theoretical values. Additional confirmation of this scheme of ionisation for the complex salts is afforded by the isolation of the intermediate products $R[MoOCl_4,H_2O]$, $R[MoO_2Cl_2,2H_2O]$, and an oxychloride, $[Mo_2O_4(OH)Cl,4H_2O]$, which may be considered as derived from the intermediate substances $[MoO_2Cl,3H_2O]$ and $[MoO_2(OH),3H_2O]$.

Salts of the Type $R[MoOCl_4,H_2O]$.

Hitherto only bromides of this type of co-ordination compound have been isolated. The first chloride of this type, *monotrimethylammonium molybdenyl tetrachloride*, was obtained as follows:

75 C.c. of the molybdenum trioxide solution, electrolytically reduced to the quinquevalent stage, were concentrated on a water-bath under diminished pressure to 20—25 c.c. 30 C.c. of a solution of trimethylamine hydrochloride (11 g.) were now admitted by releasing the vacuum, and the mixture was heated to boiling under diminished pressure. The solution was then saturated with hydrogen chloride while it was being cooled, finally in a freezing-mixture, and the emerald-green crystals thus obtained were filtered, washed with

concentrated hydrochloric acid, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide {Found: Mo, 28·8; Cl, 42·6; N, 4·24; C, 10·8; H, 3·67. $(CH_3)_3NH[MoOCl_4,H_2O]$ requires Mo, 28·9; Cl, 42·7; N, 4·22; C, 10·9; H, 3·62%}.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1·940	0·0585	6·97	47·60
0·787	0·0237	7·05	47·07
0·199	0·0060	8·07	41·13

M of $(CH_3)_3NH[MoOCl_4,H_2O]$ = 331·8.

Molecular Conductivities.

v	35·6	71·2	142·4	284·8	569·6	1139·2	2278·4	4556·8
μ	580	614	657	706	773	832	849	874

The calculated value for μ_∞ at 0° is *ca.* 880 on the scheme of ionisation and hydrolysis previously outlined, for there are produced 1 trimethylammonium, 4 chlorine, and 3 hydrogen ions, whilst the osmotic factor should be 9. The experimental results are clearly in accordance with the theoretical predictions.

Salts of the Type $[MoO_2X_2,2H_2O]R$.

In the scheme of ionisation proposed for the complex salts of quinquevalent molybdenum, the co-ordination compound $[MoO_2Cl_2,2H_2O]H$ was postulated as an intermediate product. Although this acid has not been isolated, its derivatives have been obtained in reactions involving the green complex salts.

Barium Oxalomolybdite.—Bailhache (*Bull Soc. chim.*, 1903, **68**, 161) prepared this compound by reducing ammonium molybdate in hydrochloric acid with red phosphorus, and formulated it as $BaH_2(MoO)_2(OH)_6(C_2O_4)_2,H_2O$. Viewed in the light of Werner's co-ordination theory, however, a more rational formulation and name for the substance are obtained if the molybdenum is assigned a co-ordination number of six. The new formula $Ba[MoO_2(C_2O_4),2H_2O]_2,H_2O$ clearly shows the relationship to the co-ordination compound $H[MoO_2Cl_2,2H_2O]$, and requires the name barium molybdenum dioxyoxalate. The probable correctness of this formulation and the importance of this salt can be appreciated from Bailhache's statement (*loc. cit.*) that it is produced when diammonium molybdenyl pentachloride is treated with oxalic acid and barium chloride. No details of the method were given, but experiments showed that the salt could be satisfactorily isolated by the following method:

30 C.c. of an aqueous solution of oxalic acid (1·2 g.) were added to 30 c.c. of a solution of diammonium molybdenyl pentachloride (3·5 g.), and the mixture was warmed. To the dark red solution produced, barium chloride (1·1 g.) in 60 c.c. of water was added, and on boiling, with constant stirring, a red, crystalline solid separated in good yield, which was washed with warm water and dried; it proved to be the required compound {Found: Ba, 20·8; Mo, 29·0; C, 7·28; H, 1·50. Calc. for $Ba[MoO_2(C_2O_4),2H_2O]_2,H_2O$: Ba, 20·8; Mo, 29·1; C, 7·25; H, 1·52%}.

Pyridinium Molybdenum Dioxydichloride.—Sand and Burger (*loc. cit.*) noticed that when their green pyridinium molybdenyl pentachloride was boiled with alcohol, copper-red crystals separated on cooling. This compound contained Mo, 31·7; Cl, 23·68; N, 4·75; C, 22·05; H, 2·90%, and it was assigned the formula $Mo(OH)_3Cl_2,C_5H_5N$, which requires Mo, 32·32; Cl, 23·09; N, 4·71; C, 20·20; H, 2·69%. Although the analytical figures do not show very close agreement with those demanded by theory, yet the empirical formula assigned to the substance by Sand and Burger has now been shown to be correct. It should be written, however, as $C_5H_6N[MoO_2Cl_2,H_2O]$, whereby it is characterised as the pyridinium salt of the acid $H[MoO_2Cl_2,2H_2O]$. A pure product was obtained by the following method: Freshly prepared dipyridinium molybdenyl pentachloride was added to boiling alcohol (95%) until the solution turned dark red and further solid dissolved with difficulty. On filtering and allowing the clear liquid to cool, a light red substance separated which gave Mo : Cl = 1 : 2·1 and proved to be an impure product. This was removed, and the mother-liquor, on concentration to small bulk and cooling, gave copper-red needles, which were washed with alcohol (95%) and dried in a vacuum over phosphoric oxide. The water content of the crystals varied with different samples, whilst the colour deepened with increasing water content (Found: Mo, 33·88; Cl, 24·97; N, 4·93; C, 21·5; H, 2·34. Calc. for $C_5H_6N[MoO_2Cl_2],0·25H_2O$: Mo, 33·88; Cl, 25·02; N, 4·94; C, 21·2; H, 2·29%). That this pyridinium salt and barium molybdenum dioxyoxalate are similarly constituted is readily demonstrated as follows: 3 G. of pyridinium molybdenum dioxydichloride in 50 c.c. of water were warmed with an aqueous solution of oxalic acid (1·2 g. in 30 c.c.). 1·1 G. of barium chloride in 60 c.c. of water were now added and the mixture was heated to boiling. The corresponding barium compound separated in good yield (Found: Ba, 21·4; Mo, 29·7. Calc. for $Ba[MoO_2(C_2O_4),2H_2O]_2$: Ba, 21·4; Mo, 29·9%). It will be noticed that the water content is less than that in the sample prepared from the green complex salt.

Molecular-weight Determinations.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
2·489	0·0838	3·45	86·06
1·148	0·0387	3·73	79·60
0·692	0·0233	3·90	76·12
0·222	0·0075	4·82	61·60

M for $C_5H_6N[MoO_2Cl_2,H_2O]$ = 296·9.

Molecular Conductivity.—This was determined at 0°:

v	20·56	41·12	164·5	329	1316
μ	185	210·6	275·1	312·0	336·0

These two results find an adequate explanation on the assumption that in aqueous solution the pyridinium salt undergoes ionisation and hydrolysis in accordance with the scheme:

$$[MoO_2Cl_2,2H_2O]C_5H_6N + H_2O \rightleftharpoons C_5H_6NCl + [MoO_2Cl,3H_2O]$$
$$\rightleftharpoons C_5H_6N^{\cdot} + Cl' + [MoO_2Cl,3H_2O],$$
$$[MoO_2Cl,3H_2O] + H_2O \rightleftharpoons [MoO_2(OH),3H_2O] + H^{\cdot} + Cl'.$$

Hereby, in dilute solutions, an osmotic factor of 5 should be obtained, whilst conductivity measurements, due to a pyridinium ion, 2 chlorine ions, and 1 hydrogen ion, should give μ_∞ = approx. 327·6. The experimental results are in close agreement with the theoretical values and support the scheme of hydrolysis outlined above.

Dimolybdenum Tetraoxyhydroxychloride.—The isolation of this salt, $Mo_2O_4(OH)Cl$, formed an important link in the chain of evidence for the scheme of ionisation and hydrolysis proposed for the green complex salts.

Preparation. The reddish-brown solution of quinquevalent molybdenum, obtained by the electrolytic reduction of 150 c.c. of molybdic acid solution, was concentrated on a water-bath under diminished pressure until a dark, viscous mass was obtained. Pure, dry acetone was admitted in small portions with frequent shaking and warming, until the mass just dissolved, giving a deep brown solution. This was poured with constant stirring into a large volume of dry ether and a bulky reddish-brown precipitate separated, which was washed with dry ether and kept over solid potassium hydroxide in a vacuum [Found: Mo, 51·6; Cl, 9·54; Mo : Cl = 2 : 1. $Mo_2O_4(OH)Cl,3{\cdot}5H_2O$ requires Mo, 51·7; Cl, 9·55%].

Valency. A solution of the compound in dilute sulphuric acid was titrated with standard permanganate according to Reinhardt's method, and required t_1 c.c. A solution of the same concentration was passed through the reductor (J., 1923, **123**, 969) and required

t_2 c.c. of permanganate. The valency is given by $(6 - 3t_1/t_2)$. Found: $t_1 = 7{\cdot}58$ c.c.; $t_2 = 22{\cdot}79$ c.c. Hence the molybdenum is quinquevalent.

Properties. The new chloride is a reddish-brown powder, readily soluble in water and in alcohol, giving deep reddish-brown solutions which on dilution become bright yellow. The aqueous solution is acid to litmus and reduces solutions of silver salts. The brown aqueous or alcoholic solutions of the compound turn emerald-green on saturation with hydrogen chloride, and complex salts of the type R_2MoOCl_5 may be isolated from them. On heating, the chloride decomposes with evolution of hydrogen chloride.

Molecular-weight Determinations.—These were determined in air-free water.

G. of substance per 100 g. of water.	Conc. (mol. per 1,000 g. water).	Osmotic factor.	Apparent mol. wt.
1·193	0·0314	1·85	205·7
0·656	0·0172	2·03	187·5
0·483	0·0127	2·41	157·9

M for $Mo_2O_4(OH)Cl,4H_2O = 380{\cdot}5$.

These results indicate that two ions are present in the more concentrated solutions and three individuals in the more dilute. This is satisfactorily explained by the progressive hydrolysis

$$[Mo_2O_4(OH)Cl] + H_2O \rightleftharpoons [Mo_2O_4(OH),H_2O]Cl \rightleftharpoons [Mo_2O_4(OH),H_2O]^{\cdot} + Cl',$$

or $$[Mo_2O_4(OH)Cl] + H_2O \rightleftharpoons [Mo_2O_4(OH)_2] + H^{\cdot} + Cl'.$$

Conclusions.

The results obtained from the determinations of molecular weights and molecular conductivities of a wide range of co-ordination compounds of the formula $R_2[MoOCl_5]$ leave little doubt that the scheme of hydrolysis and ionisation outlined in this paper substantially explains their behaviour in aqueous solution. It receives added support from the physico-chemical measurements made with compounds typical of the intermediate stages of the hydrolysis. Still more convincing proof of the correctness of the scheme is that it allows the formulation and characterisation of salts previously known, and derived from the green complex salts, but which had hitherto lacked systematisation. In a paper by Scagliarini (*Atti R. Accad. Lincei*, 1925, **1**, 676), the isolation of two salts, formulated as $MoOCl_3,C_5H_5N$ and $2\left[(NH_4)_2\left\{Mo\begin{matrix}(OH)_4\\Cl_3\end{matrix}\right\}\right] + C_6H_{12}N_4,HCl$, by

reactions involving the complex salt $(NH_4)_2[MoOCl_5]$ has been made the basis of the following scheme of hydrolytic decomposition :

$$R_2MoOCl_5 + H_2O = R_2Mo(OH)_2Cl_5 \xrightarrow{H_2O} R_2Mo(OH)_3Cl_4 + HCl \xrightarrow{H_2O}$$
$$R_2Mo(OH)_4Cl_3 + HCl \xrightarrow{H_2O} R_2Mo(OH)_5Cl_2 + HCl \xrightarrow{H_2O}$$
$$R_2Mo(OH)_6Cl + HCl.$$

Such a scheme does not adequately explain the physico-chemical results obtained in the present paper, nor does it elucidate the constitution of intermediate products, which are assigned co-ordination numbers of 7. The analyses quoted by Scagliarini (*loc. cit.*) for the compounds he isolated involve only determinations of molybdenum, chlorine, and nitrogen, and do not show very satisfactory agreement with the calculated values. Confirmation of the isolation of the salt $MoOCl_3,C_5H_5N$ would be of interest, for as yet $MoOCl_3$ has not been obtained.

The authors wish to express their thanks to the Chemical Society and the University of Birmingham Research Committee for grants in aid of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCLXXXVI.—*The Routine Preparation of Low-conductivity Water.*

By GUY D. BENGOUGH, JOHN M. STUART, and ALFRED R. LEE.

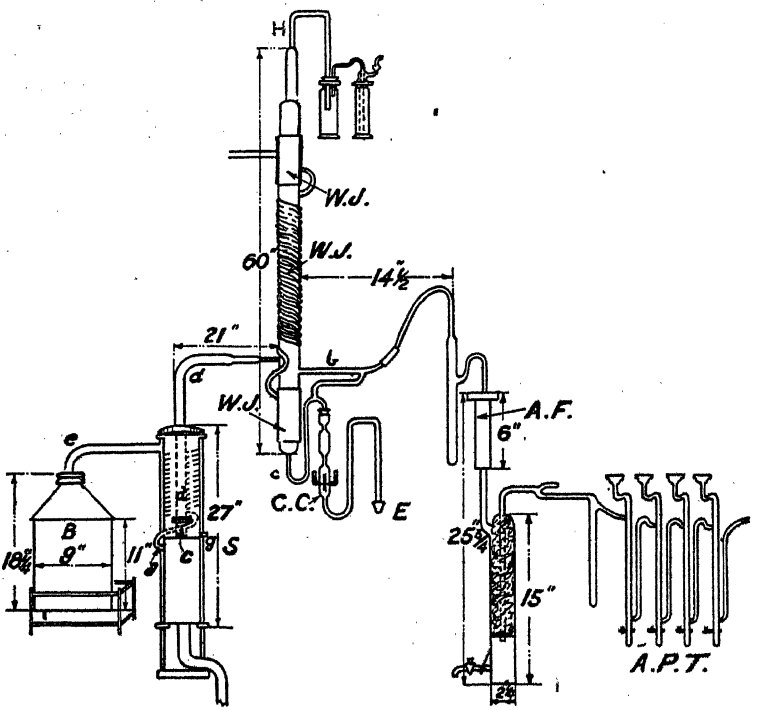
THE present communication gives details of improvements in the construction of Bourdillon's still for conductivity water (J., 1913, **103**, 791), by which it has been found possible to produce a large daily supply of such water of high quality.

Bourdillon's still delivered 7—8 litres of 0·2 gemmho conductivity in a single distillation from Oxford tap-water, and, although even the best water obtained showed conductivities as high as 0·11 gemmho from tap-water and 0·09 from distilled water at 18°, the authors constructed a precisely similar still with a view to effect improvements.

The water from this still sometimes had conductivities similar to those obtained by Bourdillon, but a regular daily supply did not maintain this degree of purity for any considerable period, even with frequent attention to small adjustments. The causes of the rises in conductivity appeared to be (*a*) minute air-leaks in some parts of the apparatus, *e.g.*, round the rubber stoppers, (*b*) inadequate trap-

ping of spray, or (c) "creeping" of water from the trap to the condenser. Air-leaks generally occurred between the spray-trap and the rest of the apparatus even when the rubber stoppers used by Bourdillon were replaced by pipe-unions, and "creeping" of water took place to a surprising extent, especially when there were considerable fluctuations of pressure in the still.

FIG. 1.



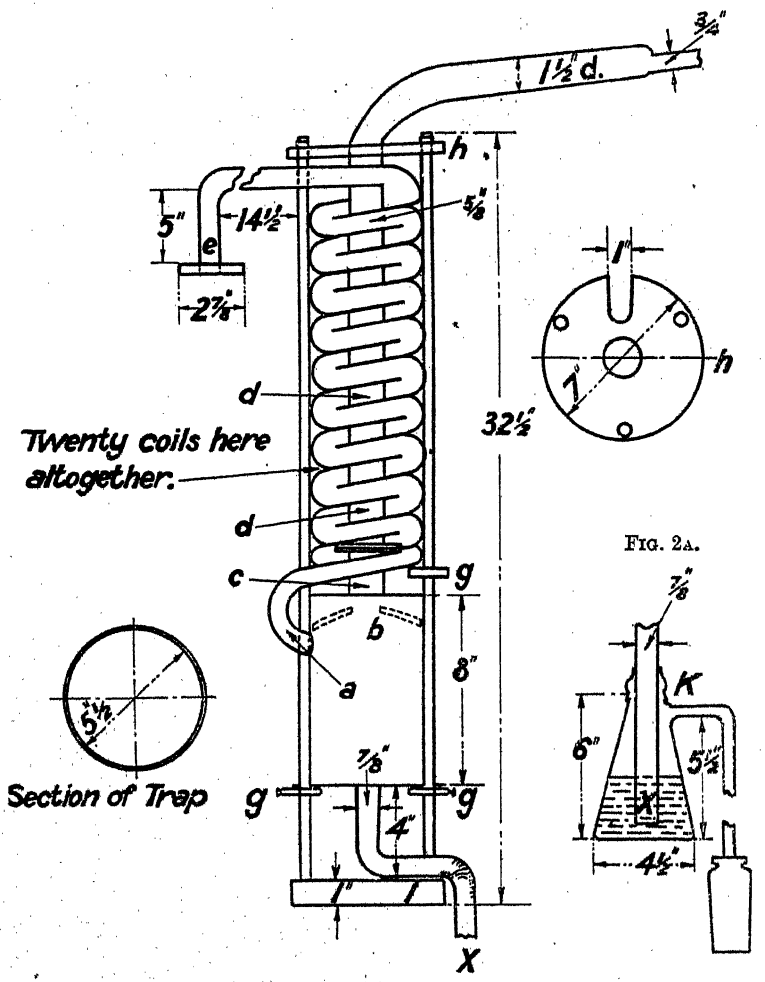
B. Boiler.
S. Spray trap.
W.J. Water jacket and cooling coils.
C.C. Conductivity cell.
A.F. Air filter.
A.P.T. Air purification train.
E. Outlet for purified water.

To eliminate these causes of trouble, the whole of that part of the still between the boiler and the block-tin condenser was redesigned; at the same time, some improvements were made in the air-purification train. The still in its final form is shown in Fig. 1.

The boiler, *B*, is made of 18-gauge (1·2 mm. thick) copper sheet, tinned on the inside. It is connected to the rest of the apparatus by two circular flanges, 7·0 cm. in diameter, soldered both to it and to the copper pipe, *e*. A ring of "hallite" packing is used between the flanges, which are held together by six bolts. (A

flange is shown in Fig. 2, *e*.) The boiler holds 10 litres of water, which is introduced, together with the ground potassium bisulphate, by separating the flanges. This is the only joint on the still that

FIG. 2.



Dimensioned sketch (not drawn to scale).

need be broken during several months' running. The available waters were a hard London tap-water, and a supply which contained traces of oil. The former was objectionable owing to the possible formation of heavy boiler-scale, so the latter was used

after a preliminary rough distillation with potassium permanganate and caustic potash in a simple form of still.

From the boiler, the steam passes through the copper tube, *e* (Figs. 1 and 2), to the trap, which has been redesigned and very solidly constructed, as shown on an enlarged scale in Fig. 2. The tube, *e*, is of 1·3 cm. internal diameter and is bent into 20 coils each of 12·5 cm. diameter, and its end is brazed into the copper trap tangentially so as to give circular motion to the steam entering the trap at *a*. A circular conical baffle-plate, *b*, is inserted above this. The steam outlet at *c* is provided with a 7 cm. circular flange (not shown in Fig. 2) which is bolted to "hallite" jointing and a similar flange on the block-tin tube, *d*. This tube has an internal diameter of 4 cm. and is soldered to the condenser. The ample width of this tube prevents any trapping of water; in the earlier still, a long, narrow, coiled tube was used and arranged outside the copper coil, but water occasionally accumulated in the bends and caused violent fluctuations of pressure in the still.

The copper coil and trap are lagged with cotton waste and asbestos sheet and are held in place by three adjustable supports, *g*, which can be clamped to three vertical brass rods. These brass rods are rigidly fixed into a heavy cast iron base, *I* (Fig. 2).

A brass plate, *h*, is bolted to the tops of the rods, and, together with a flange, provides support for the central tin tube. At first, the water from the submerged outlet tube, *X* (Fig. 2), was merely allowed to run into an open beaker, but the best water was not obtained until a definite air-trap and non-return valve were used, as shown in Fig. 2A.

The main block-tin condensing column is similar to that of Bourdillon, but the arrangements at the lower end have been altered as shown in Fig. 1; *d* is the steam inlet leading from the trap and is soldered into the main column, *b* is the inlet for purified air, and *c* the outlet for the conductivity water; *W.J.* consists of two glass water-jackets connected together by a long coil of compo-tubing carrying a stream of water. The conductivity-measuring vessel *C.C.* is fixed on to *c* by a rubber stopper. The advantage of this arrangement is that the water does not become saturated with air in the cold as in Bourdillon's method, and consequently air-bubbles do not form on the electrodes of the conductivity cells.

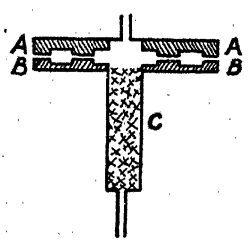
On the upper part of the tin condenser is a narrow tin tube, *H*, soldered to the main column and joined by a rubber connexion to a glass tube leading into a bottle. A second bottle is connected so that the escaping air bubbles out through a shallow layer of distilled water. If a sudden diminution of pressure occurred in the

still, the water in the second bottle would merely be sucked back into the first and not into the still.

The rate at which bubbles pass through the water serves as a rough indication that the purified air is passing satisfactorily through the still. Before distillation is stopped, the second bottle should be replaced by a soda–lime tube.

The Weiland purification trains, *A.P.T.* in Fig. 1, contain *N*-sulphuric acid, caustic potash solution, and distilled water; two are used in parallel, as it was found advisable to use a much faster stream of air than that used by Bourdillon. Recently Weiland's design has been modified: the columns containing the glass beads are now 2·5 cm. in diameter and are pinched in near the tops to retain the beads; the funnels and taps have been increased in size. The air passes through a dust-filter (*A.F.*, Fig. 1) constructed as shown in Fig. 3. This filter is a modification of one described in the Meteorological Office Report of the Advisory Committee on Atmospheric Pollution, 1916—17. It is constructed of brass, and the air first passes through the tube *C*, which is filled with special jewellers' wool, and then through a disc of special blotting paper (Ford 428 Mill) inserted between brass discs *A* and *B*, which have circular and radial grooves cut in them as shown. *A* and *B* are bolted together and the joint is waxed over externally.

FIG. 3.



The course of an actual distillation was as follows: Ten litres of laboratory distilled water were placed in the boiler with 20 g. of powdered potassium bisulphate, and heated to boiling; the "hallite" joint softened in the steam, and the boiler was then connected with the still.

The heating was adjusted so that the conductivity cell was filled and emptied every 9 or 10 minutes. This rate of delivery corresponds to the production of about 0·75 litre of water per hour and should not be greatly exceeded; if the still is run too rapidly, a trace of spray seems to get into the condenser during distillation.

The conductivity of the water was determined by the standard bridge method, a galvanometer being used to detect the zero position. This was possible because the conductivity was so low that only very small currents passed, and polarisation effects were negligible. The cells in which measurements were made were standardised with *N*/50-solutions of potassium chloride. The possible errors in the values for conductivities given in Table I are within $\pm$ 5%. The table gives the values (in gemmhos) of the specific conductivity, κ,

of each batch of water reaching the conductivity cell in a typical run of the still, the purified air being supplied at a rate of about 22·5 litres per hour, and the temperature of the water being about 15°.

TABLE I.

Batch No.	κ.	Batch No.	κ.	Batch No.	κ.	Batch No.	κ.
1	0·17	10	0·057	19	0·055	28	0·054
2	0·13	11	0·055	20	0·055	29	0·055
3	0·078	12	0·062	21	0·055	30	0·059
4	0·077	13	0·057	22	0·055	31	0·063
5	0·062	14	0·052	23	0·054	32	0·067
6	0·059	15	0·050	24	0·054	33	0·071
7	0·055	16	0·052	25	0·054	34	0·084
8	0·072	17	0·054	26	0·065		
9	0·059	18	0·055	27	0·054		

Batches 3—33 inclusive, amounted to 4040 c.c. The volume of waste water collected at the "run off" from the steam trap was 2485 c.c.

In other runs, conductivities as low as 0·045 gemmho at 18° have been obtained. This figure is not much inferior to the best values of Kohlrausch and Heydweiller (0·040 at 18°) (*Pogg. Ann.*, 1894, **53**, 223) who distilled in a vacuum in an apparatus which was only adapted to give a small quantity of the purified water. The authors' still has been in constant use for more than 2 years and requires very little attention other than the periodic renewal of the solutions in the air-purification train. It will regularly produce about four litres a day of water with a conductivity of about 0·065 gemmho.

The authors wish to express their grateful thanks to Mr. H. R. Raikes, who placed his great experience at their disposal when constructing both the still and the apparatus for measuring conductivities.

The work was carried out in the Metallurgical Laboratory of the Royal School of Mines, as part of a research directed by the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the authors wish to thank the Chairman, Professor H. C. H. Carpenter, for the many facilities afforded.

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CCLXXXVII.—*The Action of Bromine on Dimethylpyrone.*

By JOHN NORMAN COLLIE and LOUIS KLEIN.

THE constitution of the pyrone nucleus is of importance in that many interesting compounds are derived from it. Bromine reacts with it at once, but does not give ordinary addition products, and similarly there is no indication that any ethylenic linkages are present in dimethylpyrone.

10 G. of dimethylpyrone (1 mol.) and 13 g. of bromine (1 mol.) were allowed to react in chloroform solution, and the mixture became orange-coloured and slightly warm. The solvent was evaporated at the ordinary temperature, and the resulting bright orange-coloured, crystalline solid was washed with water, which removed dimethylpyrone hydrobromide, together with a small quantity of some pyrone compound containing bromine—this was probably the bromodimethylpyrone, but owing to its high solubility it could not be separated from the hydrobromide.

The orange compound (yield, 10 g.) was best recrystallised from acetic acid or chloroform; m. p. 136° (Found: C, 34·1; H, 3·8; Br, 49·5; *M*, cryoscopic in naphthalene, 456, 479. Calc. for $C_{14}H_{17}O_4Br_3$: C, 34·4; H, 3·5; Br, 49·1%; *M*, 489).

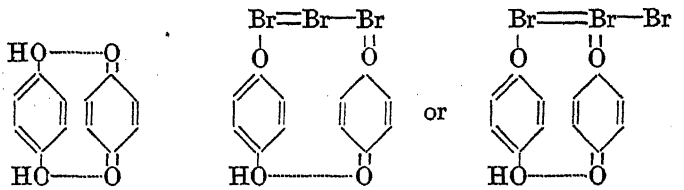
This compound has also been obtained by Hantzsch and Denstorff (*Annalen*, 1906, **349**, 39), who only gave a bromine determination, by the action of bromine on dimethylpyrone hydrobromide. They recognised it as a perbromide, and we have confirmed this by obtaining several characteristic reactions for perbromides, some of which were carried out quantitatively, although in the reaction with ammonia only about two-thirds of the theoretical amount of nitrogen were evolved.

On being warmed with water, the compound loses its colour and dissolves, except for a small quantity of a yellow oil (Found: ionisable Br, 37·0%). On standing with water for 3 days, however, only a trace of the yellow oil remained, and the ionisable bromine was then 46·9%. The yellow *oil* does not crystallise on keeping and cannot be distilled (Found: Br, 58·1. $C_7H_6O_2Br_2$ requires Br, 56·7%). Aqueous potassium hydroxide behaves in a similar manner to water (Found: ionisable Br, 46·1%).

The action of heat on the orange compound is complex. If kept just at its m. p. it loses colour, and then solidifies on cooling. If more strongly heated, it chars and gives off hydrogen bromide, the product being almost entirely soluble in water, and consisting chiefly of dimethylpyrone hydrobromide, mixed with a small

quantity of (probably) the bromodimethylpyrone, which, however, could not be separated. The small amount of insoluble *substance* was a yellow, non-crystallisable oil (Found : Br, 61·4%).

The orange compound resembles quinhydrone in some respects, *e.g.*, reaction with water and possession of colour, and this suggests a similarity in molecular constitution :



The action of a larger amount of bromine on dimethylpyrone was tried : 10 g. of the pyrone and 26 g. of bromine in chloroform solution. After evaporation of the chloroform, the residue was treated with water, and the insoluble portion recrystallised from dilute alcohol. A colourless compound resulted; m. p. 163° (Found : C, 29·8; H, 2·6; Br, 56·3. Calc. for $C_7H_6O_2Br_2$: C, 29·8; H, 2·1; Br, 56·7%). This compound had been previously obtained by Feist and Baum (*Ber.*, 1905, **38**, 3562). On being boiled with water it gives bromoacetone. It does not form salts with acids, and its solution in alcohol does not give an immediate precipitate with silver nitrate. On being heated with sodium ethoxide solution, it turns deep red in colour.

If excess of bromine is allowed to react with dimethylpyrone in the absence of a solvent, the mixture becomes warm, and on boiling it evolves hydrogen bromide and eventually becomes solid. Extraction with alcohol leaves a crystalline residue, which is almost insoluble in most solvents. From hot acetic anhydride, however, a *substance* separates in bunches of needles, m. p. 229° (darkening at 227°) (Found : C, 19·3; H, 1·2; Br, 71·5. $C_7H_4O_2Br_4$ requires C, 19·1; H, 0·9; Br, 72·7%). This compound is very stable, being unaffected by metallic sodium in boiling benzene solution, or by warm concentrated sulphuric or nitric acids, from solutions in which it is precipitated unchanged on the addition of water. Heating with ammonia in a sealed tube at 140° or boiling with sodium hydroxide solution, however, effect decomposition, which is very far-reaching in the former case.

A curious iodine compound was obtained by one of the authors (J., 1900, **77**, 1116; 1921, **119**, 1550) by the action of iodine on the barium salt of diacetylacetone. Bromine has now been found to give a similar compound; it was added slowly with shaking to an aqueous suspension of the barium salt (45 g.), and dilute hydro-

chloric acid then precipitated 9 g. of the *substance*, which was recrystallised from dilute alcohol; m. p. 106°; b. p. *ca.* 310° (decomp.) (Found: C, 38·6; H, 3·4; Br, 36·6. *M*, microcryoscopic in camphor, 236. $C_7H_7O_3Br$ requires C, 38·4; H, 3·2; Br, 36·5%; *M*, 219). In all its reactions it resembles the iodine compound. It can be boiled with the strongest sodium hydroxide, or with sodium ethoxide, without decomposition, and is reprecipitated on adding an acid. Cold concentrated sulphuric acid does not decompose it, and although it does not react with cold sodium carbonate solution, on warming, carbon dioxide is evolved. With bleaching-powder solution, it gives a precipitate of calcium carbonate. With ferric chloride, it gives a red precipitate. It can also be made by the action of bromine on the sodium salt of diacetylacetone. It forms a *monobenzoyl* derivative, m. p. 112° (Found: C, 51·8; H, 3·7; Br, 24·5. $C_{14}H_{11}O_4Br$ requires C, 52·0; H, 3·4; Br, 24·8%); and with phenylhydrazine it yields a *compound*, m. p. 142° (decomp.) (Found: N, 8·8; Br, 26·3. $C_{13}H_{13}O_2N_2Br$ requires N, 9·1; Br, 25·9%).

An unsuccessful attempt was made to produce a corresponding chlorine compound by the action of chlorine on the barium salt of dimethyl pyrone.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, June 30th*, 1927.]

CCLXXXVIII.—*The Application of the Hydrogen Electrode to Organic Bases: Piperidine, and its Use as an Alkaline Buffer.*

By EDMUND B. R. PRIDEAUX and FRANK L. GILBERT.

THE dissociation constants of organic bases rest on conductivity determinations alone, whilst the hydrogen-ion concentrations of their partly neutralised solutions are either calculated from these constants or determined by colorimetric methods. It would seem desirable to test these results with the hydrogen electrode, as has been done in the case of acids. It has long been known that this electrode is untrustworthy with ammonia and some amines (Bottger, *Z. physikal. Chem.*, 1899, **24**, 253), and it has also been stated (Kolthoff, *Biochem. Z.*, 1925, **162**, 289) that the alkaloids are susceptible to catalytic reduction at the surface of a hydrogen electrode. The possibility of carrying out an electrometric titration on hydrazine has, however, been established by Gilbert (*J. Amer. Chem. Soc.*, 1924, **46**, 2648). This base is unstable in most respects, but is resistant to reducing agents. Although the numerical results

were not given in the paper, one can infer that the first constant was in fairly good agreement with the value, 3×10^{-6}, based on Bredig's measurements of conductivity.

Piperidine seemed to be eminently suitable for testing the constant derived from conductivity, since it is a moderately strong base which obeys the dilution law, and it was deemed to be stable towards platinum–hydrogen. The dissociation constant according to Bredig is $1{\cdot}6 \times 10^{-3}$, and $\lambda_0 = 216$, expressed in modern units (*Z. physikal. Chem.*, 1894, **13**, 191). The value used by Hantzsch and Sebaldt (*ibid.*, 1900, **33**, 129) is 232 at 25°. In the case of the hydrochloride, at $v = 1024$, $\lambda = 110$; if 2·5 units be added, according to the usual rule, $\lambda_0 = 112{\cdot}5$; since the mobility of the chlorine ion is 75·5, that of the piperidinium ion is 37·0, and, that of the hydroxyl ion being 196, λ_0 for piperidine is found to be 233. On combining this with the λ values of Bredig (converted into ohms) for $v = 32$ and 256, one finds $K = 1{\cdot}42 \times 10^{-3}$ and $1{\cdot}30 \times 10^{-3}$, respectively. These are rather higher than the constants of Hantzsch and Sebaldt (*loc. cit.*), *viz.* :

Temp.	=	15°	20°	25°
10^3K	=	1·11	1·15	1·20

from which, by interpolation, the constant at 18° is $1{\cdot}14 \times 10^{-3}$, $p_K = 2{\cdot}94$. We consider this constant to be a more satisfactory basis for calculations than the uncorrected constant of Bredig. We have tested its validity for expressing the p_H values obtained during neutralisation by (*a*) a potentiometric and (*b*) a colorimetric titration.

(a) *Electrometric Titration.*—The usual circuit for potentiometric titrations was set up, containing a cadmium cell, which was checked against an N.P.L. Standard, a capillary electrometer, and a metre slide wire, which had been calibrated against an accurate resistance box. A platinised platinum–hydrogen electrode of the Hildebrand type dipped into an open beaker which contained the solution of piperidine. The other half-cell was an N/10-potassium chloride–calomel electrode, the two solutions being connected by a salt bridge of saturated potassium chloride–agar.

To the N/10-piperidine solution, N-hydrochloric acid was added with stirring. The balance point on the bridge-wire became steady at once, and readings were taken after each addition of acid. The *E.M.F.*, E_c in table, of the hydrogen half-cell against an electrode in N-hydrogen ion is equal to the *E.M.F.*, E in table, corresponding to the balance-point minus 0·338. The readings are given as c.c. of hydrochloric acid added to a given volume of piperidine :

c.c.	=	2·1	2·45	2·75	3·0	3·2	3·4
E	=	0·962	0·943	0·914	0·845	0·502	0·461
E_c	=	0·624	0·605	0·576	0·507	0·164	0·123

$\Delta E/\Delta C$ assumes a high value between 3·0 and 3·2 c.c.; the subsequent readings correspond to solutions beyond the equivalence point.

The possibility of a satisfactory electrometric titration is thus demonstrated. Some of these results were used in determining p_K (see below), the following p_H values being calculated from $E_c/0{\cdot}058$:

E_c =	0·624	0·605	0·576	0·507	0·164	0·123
p_H =	10·75	10·45	9·92	8·73	2·84	2·12

Electrometric Determination of K.—Since the middle part of the neutralisation is of particular importance in determining K, another experiment was carried out (with a different volume of piperidine) from an earlier stage in the neutralisation and with 0·55N-acid, in order to obtain a greater accuracy in the values of x, the fraction of base neutralised. The values of p_K are calculated from the equation

$$p_K = \log (1 - x)/x + p_{K_W} - p_H,$$

where p_{K_W} has its usual significance and is equal to 14·13 at 18°.

The potentiometric titration of 0·1N-piperidine with 0·55N-hydrochloric acid.

HCl (c.c.).	E_c.	p_H.	100x.	p_K.	HCl (c.c.).	E_c.	p_H.	100x.	p_K.
0·65	0·682	11·8	17·8	2·99	2·10	0·637	10·95	57·4	3·05
0·95	0·672	11·6	26·0	2·98	2·40	0·620	10·75	66·0	3·09
1·24	0·665	11·43	33·9	2·99	2·65	0·607	10·55	73·3	3·14
1·60	0·652	11·23	43·7	3·00		0·605	10·45	80	3·09
1·85	0·645	11·1	51·0	3·01		0·576	9·92	90	3·26
1·95	0·640	11·05	53·4	3·02					

Thus the potentiometric constant is distinctly lower (p_K higher) than that derived from conductivity results; the constancy is very satisfactory, the trend up to $x = 0{\cdot}50$ being very slight, less indeed than in the case of most acids. Thus it has been shown by Michaelis and Kruger (*Biochem. Z.*, 1921, **119**, 307) that the p_K of acetic acid when 50% neutralised is 4·665, whilst that of the free acid is 4·733; there is therefore a decrease of 0·068 in p_K, or an increase in the constant. Although it is not possible to determine the potentiometric p_K with sufficient accuracy on aqueous solutions of free piperidine, we do know that the change of p_K over a large range of neutralisation is only about 0·02. If, however, p_K of the pure base is 2·94, the difference between this and the value prevailing at 50% neutralisation is 0·07—of the same order as the difference for acetic acid, but in the opposite direction. While, therefore, the constant increases during neutralisation in the case of typical weak acids, it decreases in the case of this weak base. It is intended to test other bases,

in order to find whether this behaviour is characteristic of the class.

The increases in the constants of acids may be plausibly attributed to the presence of the increasing amount of salt formed during the neutralisation, since the addition of sodium chloride, or other neutral salt, has a marked effect in the same direction (Michaelis and Kruger, *loc. cit.*).

The present effect, however, is not a salt effect, as was proved by the following experiments. Sodium chloride was added to the solutions under investigation so as to preserve a constant concentration of chloride, equal to that which would have been attained at the end of the neutralisation. Had the drift in the constant been a salt effect, the balance point would have been altered in the first stages of neutralisation, so as to give a constant p_K equal to the slightly higher value obtained in the nearly neutralised solution.

Addition of NaCl to 30 c.c. of piperidine at various degrees of neutralisation.

100 x.	Balance point on bridge, without NaCl.	Weight of NaCl added (g.).	Balance point in presence of NaCl.
10	51·2	0·158	51·2
30	49·7	0·117	49·8
50	48·7	0·088	48·7
80	46·4	0·035	46·5

Hence the *E.M.F.*'s and the p_H values are not affected by moderate amounts of neutral salt, the presence of which, therefore, does not account for the slight trend in K in the case of solutions which are more than 50% neutralised.

(b) *Colorimetric Titration.*—It is clear from the above results that the calculation of p_H during neutralisation from the constant which is based on conductivity will give numbers about 0·2 unit higher than those determined by the hydrogen electrode. It remains to be found whether these latter p_H values have the same effect on indicators as those derived from known buffer solutions.

We have selected the buffers of Ringer : 0·15*N*-Na_2HPO_4 + 0·1*N*-NaOH (p_H 11—12), and one of Sörensen's : 0·2*N*-$Na_2B_4O_7$ + 0·1*N*-NaOH or HCl (p_H 11—8). These solutions were matched against the piperidine at various stages of neutralisation, by using the B.D.H. "universal indicator," which can be made to show changes within 0·1 in p_H over the range involved. To 10 c.c. of the *N*/10-piperidine solution were added counted numbers of drops of the 0·55*N*-hydrochloric acid, from a dropping pipette, 22 drops of which were equal to 1 c.c. When the colour matched that of the buffer solution containing the same concentration of indicator, the % of neutralisation was recorded.

No. of drops.	p_H of buffer.	$100x$.	p_K.	No. of drops.	p_H of buffer.	$100x$.	p_K.
9	11·74	22·5	2·93	35	10·05	87·5	3·23
18	11·19	45	3·02	36	9·84	90	3·33
22	11·01	55	3·03	37	9·50	92·7	3·53
33	10·33	82·5	3·12	38	9·41	95·0	3·43
34	10·15	85·0	3·23	39	9·21	97·5	3·33

The values determined by the hydrogen electrode are therefore confirmed, and the slight trend in K_B is again found, the values of p_K rising more sharply when neutralisation is nearly complete.

In all the middle part of its neutralisation interval, piperidine will make an excellent buffer solution: the p_H values may be calculated from $p_K = 3{\cdot}00 \pm 0{\cdot}02$ between 15 and 55% neutralisation. In an $N/10$-solution of piperidine which has been 50% neutralised by $0{\cdot}5N$-hydrochloric acid, p_K is found, both by the hydrogen electrode and by indicators, to be $11{\cdot}10 \pm 0{\cdot}05$. This is an accurately defined reference point for the measurement of acidity.

UNIVERSITY COLLEGE,
NOTTINGHAM.

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CCLXXXIX.—*Researches in the Menthone Series. Part V.* d-neoiso*Menthylamine.*

By JOHN READ and GEORGE JAMES ROBERTSON.

THE constitutional formula of the menthylamines admits of the existence of four optically inactive and eight optically active forms, and of these the only stereoisomerides remaining to be prepared and characterised are the *neoiso*menthylamines (compare J., 1926, 2209, 2223). Wallach (*Annalen*, 1898, **300**, 278) obtained two bases, now called *l*-menthylamine and *d-neo*menthylamine, by heating *l*-menthone with ammonium formate. We regard both these bases as derivatives of *l*-menthone (*loc. cit.*); since, however, under the conditions of the experiment *l*-menthone is transformed partly to *d-iso*menthone (this vol., p. 1278), we considered that the reaction product should contain a corresponding proportion of formylated *iso*menthylamines. By applying the knowledge already acquired of the derivatives of active forms of the three known bases, we have been able to prepare from this product a new salicylidene (*o-hydroxybenzylidene*) derivative, m. p. 99—100°, $[\alpha]_D$ — 17·9°, which must be regarded as an active form of salicylidene*neoiso*menthylamine (J., 1926, 2225).

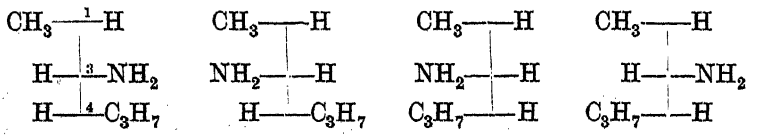
We have already shown that *d-iso*menthone, when oximated and reduced, yields *d-iso*menthylamine. *l*-Menthone yields *l*-menthyl-

amine in a similar way, and gives a mixture of *l*-menthylamine and *d-neo*menthylamine in reaction with ammonium formate. By analogy we anticipated that *d-iso*menthone would furnish *d-iso*-menthylamine and *l-neoiso*menthylamine in the last-named reaction. A careful scrutiny of the data suggests that *d-iso*menthylamine may exist in the formylated mixture, although it has not yet been isolated therefrom; the new lævorotatory salicylidene derivative, however, yielded upon hydrolysis a feebly dextrorotatory neoiso-*menthylamine*, having $[\alpha]_D + 9°$ in chloroform. The *hydrochloride* also was dextrorotatory, having $[\alpha]_D + 20{\cdot}9°$ in dilute aqueous solution. All the other derivatives, nine in number, as yet prepared from the base display rather small lævo-rotations, thus fulfilling the anticipated tendency. Since, however, the free base is dextrorotatory, we propose to name it *d-neoiso*menthylamine. The subjoined summary of melting points and specific rotatory powers indicates some of the more important relationships existing between the four optically active forms under discussion. The values of $[\alpha]_D$ were observed in water for the hydrochlorides and in chloroform for the other derivatives (compare J., 1926, 2225):

		Menthylamines.			
Derivative.		*l*-.	*d-neo*-.	*d-iso*-.	*d-neoiso*-.
Hydrochloride.	m. p.	280°	189°	250°	250°
	$[\alpha]_D$	−36·6°	+21·5°	+23·6°	+20·9°
Formyl.	m. p.	102—103	117—118	45—46	Liquid
	$[\alpha]_D$	−83·8	+53·8	+31·3	−3·9
Acetyl.	m. p.	145	169—170	77—79	99—100
	$[\alpha]_D$	−81·7	+53·0	+30·7	−2·6
Benzoyl.	m. p.	157	121·5	97—98	151
	$[\alpha]_D$	−62·8	+22·7	+18·3	−10·4
β-Naphthalene-sulphonyl.	m. p.	135	208	80—81	120
	$[\alpha]_D$	−53·3	+43·7	−2·8	−10·7
Benzylidene.	m. p.	69—70	45—46	67—68	68—69
	$[\alpha]_D$	−132·5	+61·7	+90·7	−34·2
Salicylidene.	m. p.	57—58	99—100	122	99—100
	$[\alpha]_D$	−119·2	+30·0	+77·6	−17·9

From these data it is evident that no striking general similarity exists between derivatives of the *neo*- and *neoiso*-menthylamines (compare J., 1926, 2224); further, of the four supposed benzomenthylamides described by Tutin and Kipping (J., 1904, **85**, 73) two only can now be regarded as pure substances. The data are of particular interest when considered in conjunction with the configurational scheme advanced some time ago for the menthylamines (J., 1926, 2213) and reproduced below with the amendment

that the *trans*-configuration is adopted, in place of the *cis*-, for menthone (compare this vol., p. 1278) :



l(or *d*)-Menthylamine. (I.) | *d*(or *l*)-*neo*-Menthylamine. (II.) | *d*(or *l*)-*iso*-Menthylamine. (III.) | *d*(or *l*)-*neoiso*-Menthylamine. (IV.)

The adoption of configuration (II), rather than (IV), for *d-neo*-menthylamine (J., 1926, 2213) is now supported by the fact that the sense of the optical rotation undergoes a change throughout the series of substitution derivatives in passing from (I) to (II), but not in passing from (I) to (IV). Further generalisations may also be made which appear to accord with the suggested configurational scheme. Excluding β-naphthalenesulphon-*d-iso*-menthylamide, which is only feebly active, and also the hydrochlorides, which differ from the other derivatives in being ionisable, it is remarkable that the reversal of the asymmetry of carbon atom (3), carrying the characteristic amino-group, invariably changes the sign of the optical rotation. On the other hand, the reversal of the asymmetry of either of the carbon atoms (1) or (4) does not affect the sign of the optical rotation.

With regard to numerical values, it is seen that the derivatives of *trans*-menthone (I and II) possess greater rotatory powers than the derivatives of *cis*-menthone (III and IV). The most striking numerical relationships yet observed between the optical rotatory powers of corresponding members of the four series are shown by the formyl and acetyl derivatives: the sum of (I) and (IV) is in each instance practically equal in amount, but opposite in sign, to that of (II) and (III); similar results are obtained by comparing the sum of (I) and (III) with that of (II) and (IV), and the sum of (I) and (II) with that of (III) and (IV). These relationships do not hold for the other derivatives described in this communication, but it is hoped to pursue the subject in order to ascertain whether any definite principle of optical superposition can be discerned in this remarkable series of stereoisomerides.

The action of nitrous acid on the four types of stereoisomeric menthylamines is of particular interest. It must be recognised that the configurations which have been assigned to these substances are based largely upon the assumption that the stereoisomeride which passes most readily into a particular menthol when treated with nitrous acid is configurationally similar to that

menthol, the accompanying Δ^3-menthene being attributed in such instances to the occurrence of a Walden inversion (compare J., 1926, 2213). Thus, *l*-menthylamine and *d-iso*menthylamine yield the largest proportions of *l*-menthol and *d-iso*menthol, respectively, when treated with this reagent. Accepting these processes as the normal ones, the simultaneous formation of partly racemised *d*-Δ^3-menthene takes place through a Walden inversion, leading to the intermediate production of *d-neo*menthol and an optically active *neoiso*menthol, respectively; these alcohols, since they possess a hydrogen atom (4) in the *cis*-configurative position to the hydroxyl group (3), then undergo dehydration. The formation of partly racemised *d*-Δ^3-menthene as the main product in the remaining instances of *d-neo*menthylamine and *d-neoiso*menthylamine is accordingly regarded as the normal procedure. *l*-Menthol, which we now show to be present in small amount in the product yielded by *d-neo*menthylamine, will in this instance arise by virtue of a Walden inversion, and it appears that *d-neoiso*menthylamine yields *d-iso*menthol in a similar way.

l-Menthylamine, *d-neo*menthylamine, *d-iso*menthylamine, and *d-neoiso*menthylamine may all be utilised as sources of *d*-Δ^3-menthene, in varying yields, by the action upon them of nitrous acid (compare also Tschugaeff, *Ber.*, 1899, **32**, 3333). In these changes, carbon atom (1) alone retains its asymmetry, and a proof is thus afforded that the spatial disposition of the groups about this atom is similar in the four stereoisomeric bases concerned, as indicated in our configurational scheme. An interesting distinction between the substances is provided by the observation that the salicylidene derivatives of the menthylamines and *iso*menthylamines are phototropic, while those of the *neo*menthylamines and *d-neoiso*menthylamine are not.

Experimental.

Isolation and Characterisation of d-neoiso*Menthylamine.*—The crude oily form-*d-neo*menthylamide obtained by heating *l*-menthone with ammonium formate (Wallach, *Annalen*, 1898, **300**, 283) was dried in ether solution and distilled under diminished pressure. The first fraction consisted of menthone, but 85% of the material passed over at 160—166°/9 mm. as a clear, pale yellow syrup, which yielded about 30% of its weight of crystalline form-*d-neo*menthylamide when kept overnight in contact with dry ether. After separation of the crystals by filtration and removal of the ether, the remaining syrup had $n_D^{15°}$ 1·4840 and $[\alpha]_D^{15°}$ − 21·1° in chloroform ($c = 4·3$). Examination showed that the aqueous layer formed in the reaction could be discarded.

The clear solution obtained by hydrolysing the syrup with hydrochloric acid (*Annalen*, 1893, **276**, 308) was rendered alkaline and steam-distilled; the distillate, when carefully neutralised with hydrochloric acid and evaporated to dryness, yielded a colourless, crystalline mass of a mixture of menthylamine hydrochlorides. A non-volatile part of the alkaline mixture, having b. p. 166—176°/9 mm., $[\alpha]_D^{15°}$ + 6·6°, proved to consist of unchanged formyl derivative; selective hydrolysis had thus occurred. In subsequent hydrolyses, the boiling with concentrated hydrochloric acid was therefore continued for 4—5 hours after the syrup had dissolved; the mixture of menthylamine hydrochlorides then obtained had $[\alpha]_D^{15°}$ — 4° in water (c = 5·1).

Attempts to separate the constituents of this mixture by treatment with ether, acetone, methyl alcohol, and other organic solvents yielded unsatisfactory results. Fractional extraction of the liberated base from its solution in ether by agitation with four successive equal quantities of 0·6*N*-hydrochloric acid yielded fractions of hydrochloride having $[\alpha]_D^{15°}$ — 8·4°, — 5·3°, — 4·6°, and + 1·9°, respectively, in aqueous solution (c = 4·5). A certain degree of separation was thus effected, but the best results were obtained by preparing the salicylidene derivative directly from the mixture of hydrochlorides having $[\alpha]_D^{15°}$ — 4°, described above. When recrystallised twice from light petroleum and once from alcohol, material made in this way yielded about 8% of pure *salicylidene*-d-neois*omenthylamine*. This substance forms yellow needles, m. p. 99—100°, $[\alpha]_D^{15°}$ — 17·9° in chloroform (c = 2·3). (Found: C, 78·7. $C_{17}H_{25}ON$ requires C, 78·75%). A mixture of this derivative with about an equal amount of salicylidene-*d*-*neo*menthylamine (m. p. 98—99°) melted at 74—78°.

Hydrolysis was best effected by boiling the substance (12 g.) for 3·5 hours with a mixture of sulphuric acid (8·5 c.c.) and water (72 c.c.). Salicylaldehyde was extracted with ether, and d-neois*omenthylamine hydrochloride* was then prepared by steam-distilling the basified liquid into the requisite amount of dilute hydrochloric acid. The crystalline powder obtained upon evaporation was very soluble in alcohol or water, and practically insoluble in light petroleum or ether. When dissolved in boiling acetone containing a trace of methyl alcohol, it crystallised with difficulty in fine, silky needles, which did not melt below 250°; $[\alpha]_D^{15°}$ in water (c = 3·1) was + 20·9° (Found, by titration: Cl, 18·4. $C_{10}H_{21}N,HCl$ requires Cl, 18·5%). Free d-neois*omenthylamine* is a liquid which resembles the stereoisomeric menthylamines in its odour. The approximate rotatory power was determined by extracting with chloroform the base liberated from a known weight of hydrochloride

(1·669 g.); the dried chloroform solution (50 c.c.) gave $[\alpha]_D^{15°}$ + 9° (α_D^{15} + 0·30° in a 1-dcm. tube).

The *formyl* derivative is a viscid oil, having $[\alpha]_D^{15°}$ − 3·9° in chloroform (c = 4·4). The *acetyl* derivative is very soluble in organic solvents; it crystallised from light petroleum in needles which softened at 87°, melted at 99—100°, and showed $[\alpha]_D^{15°}$ − 2·6° in chloroform (c = 2·7). The *benzoyl* derivative crystallises from alcohol in fine, silky needles, m. p. 151°, $[\alpha]_D^{15°}$ − 10·4° in chloroform (c = 2·3). The β-*naphthalenesulphonyl* derivative, after three recrystallisations from alcohol, formed hard aggregates, m. p. 120°, $[\alpha]_D^{15°}$ − 10·7° in chloroform (c = 2·9). *Benzylidene*-d-neoiso*menthylamine* separates from hot methyl alcohol in coarse, colourless needles, m. p. 68—69°, $[\alpha]_D^{15°}$ − 34·2° in chloroform (c = 2·0). A mixture with benzylidene-*l*-menthylamine (m. p. 69—70°) melted at 45—51°. d-neoiso*Menthylcarbamide* crystallised from ether–light petroleum in fine needles, m. p. 115—116°, $[\alpha]_D^{15°}$ − 3·1° in chloroform (c = 1·9). d-neoiso*Menthylphenylcarbamide* forms small needles, m. p. 149—150°, $[\alpha]_D^{15°}$ − 12·1° in chloroform (c = 2·5); the pure derivative was readily obtained in 75% yield. d-neoiso*Menthylphenylthiocarbamide* crystallises from ether–light petroleum in well-developed prisms, m. p. 99°, $[\alpha]_D^{15°}$ − 6·7° in chloroform (c = 3·0).

Action of Nitrous Acid on d-neo*Menthylamine and* d-neoiso-*Menthylamine.*—1. *d-neo*Menthylamine hydrochloride (50 g.), obtained by hydrolysing form-*d-neo*menthylamide (m. p. 114—116°), was treated with nitrous acid in the usual manner (this vol., p. 1280). The product contained tarry matter. When distilled it yielded a first fraction (16 g.) having b. p. 57—83°/11 mm., $[\alpha]_D^{15°}$ + 58·6° (in ether; c = 1·8), $n_D^{15°}$ 1·4555, and a second fraction (4·2 g.) having b. p. 83—102°/11 mm., $\alpha_D^{15°}$ − 18·12°, $[\alpha]_D^{15°}$ − 20·1°, $n_D^{15°}$ 1·4630. The latter fraction had an odour of menthol; when heated with phthalic anhydride, it yielded a product which, after two recrystallisations from light petroleum containing a little alcohol, had m. p. 111°, $[\alpha]_D^{15°}$ − 81·5° (in chloroform; c = 2·1). A mixture of this substance with *l*-menthyl hydrogen phthalate (m. p. 112—113°) melted at 111—113°; it was therefore diagnosed as slightly impure *l*-menthyl hydrogen phthalate (compare Pickard and Littlebury, J., 1912, **101**, 109).

2. *d-neoiso*Menthylamine hydrochloride (6 g.) was treated similarly, a little dilute hydrochloric acid being added during the progress of the reaction. The crude product (3 g.) when distilled yielded a first fraction (2·1 g.) having b. p. 76—109°/21 mm., $\alpha_D^{15°}$ + 17·64°, $n_D^{15°}$ 1·4591, and a second fraction (0·6 g.) having b. p. 90—100°/9 mm., $[\alpha]_D^{15°}$ + 5·5° (in alcohol; c = 3·7), $n_D^{15°}$

1·4675. The second fraction, which showed no tendency to crystallise, possessed an odour of *iso*menthol (this vol., p. 1280).

Phototropy of Salicylidenementhylamines.

Of the twelve possible stereoisomeric salicylidenementhylamines, nine have now been described, the remaining three being the derivatives of *d*-menthylamine, *l-neoiso*menthylamine, and *dl-neoiso*menthylamine. The nine stereoisomerides are all normally pale yellow in colour, but it is remarkable that certain of them display phototropy, while the others do not. When exposed for a few minutes to sunlight or to bright daylight, salicylidene-*l*-menthylamine assumes a deep orange colour, but reverts to pale yellow when kept for a while in subdued daylight or in the dark. A less pronounced change of a similar kind is exhibited by the three salicylidene*iso*menthylamines, and to a slight extent by salicylidene-*dl*-menthylamine, but the three salicylidene*neo*menthylamines and salicylidene-*d-neoiso*menthylamine are unaffected by the treatment indicated. Salicylidene-*dl*-menthylamine was originally obtained as a liquid (J., 1926, 2227), but when kept for several months it changed to a pale yellow, crystalline mass, which softened at 60° and melted indefinitely at about 80°. It is hoped in due course to undertake a more detailed study of the phototropy of these derivatives.

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UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, August 5th*, 1927.]

CCXC.—*Reactions of Sodium Compounds of Aromatic Ketones. Part I. Synthesis of Triarylcarbinols and of Triarylmethane Dyes.*

By ERNEST HARRY RODD and FRANK WILLIAM LINCH.

IT has been known for many years that aromatic ketones form compounds with metallic sodium in an inert solvent. The literature of the subject, from the original observation by Beckmann and Paul (*Annalen*, 1891, **266**, 1) that benzophenone forms a coloured compound with sodium, is usefully summarised in *Ann. Reports*, 1925, **22**, 123—126. Workers in this field have hitherto confined themselves to unsubstituted ketones such as benzophenone and phenyl diphenylyl ketone, and have studied the decomposition

products of the sodium ketyls with water, oxygen, iodine, and methyl iodide with the object of elucidating their structure. Schlenk and his co-workers state that benzophenone forms a blue monosodio-derivative, probably containing tervalent carbon, and a violet disodio-derivative, $CPh_2(ONa)Na$; the disodio-compound of phenyl diphenylyl ketone was actually isolated (*Ber.*, 1914, **47**, 487).

We were attracted by the possibility of preparing triarylmethane dyes by the interaction of the sodio-derivatives of suitably substituted ketones with halogenated aromatic compounds. The observation by Frey (*Ber.*, 1895, **28**, 2514), that triphenylcarbinol is formed from benzophenone and bromobenzene in ether in the presence of sodium, made the project appear feasible. Blicke had also observed the formation of triphenylcarbinol from benzaldehyde, bromobenzene, and sodium, and he assumed the intermediate formation of benzophenone (*J. Amer. Chem. Soc.*, 1924, **46**, 2560).

Experiments at once showed that Michler's ketone, *pp'*-tetramethyldiaminobenzophenone, when heated with chlorobenzene in the presence of sodium, gave, after treatment of the product with water, the expected carbinol, which was readily converted into the well-known dyestuff, malachite green. The formation of the sodio-compound of the ketone is extremely slow in ether on account of the low solubility of the ketone and the low b. p. of the solvent, but in benzene or toluene at 80—100° the reaction is much more rapid, and these solvents are suitable for carrying out the synthesis. The reaction has been extended to a number of chlorinated hydrocarbons, including *o*-chlorotoluene, 4-chloro-*m*-xylene, chloro-*p*-xylene, α- and β-chloronaphthalene, and chloroanisoles. In place of Michler's ketone, *pp'*-tetraethyldiaminobenzophenone has been used; with chlorobenzene, this gives the carbinol corresponding with the dye, brilliant green. The condensation of the ketone with the chloro-compound requires two atoms of sodium per mol. of ketone for its completion; by the use of this proportion, with a slight excess of chloro-compound, there is little unchanged ketone and no sodium left at the end of the reaction. The reaction may therefore be expressed by the equations:

$$R_2CO + 2Na = R_2C(ONa)Na;$$
$$R_2C(ONa)Na + R'Cl = R_2R'C(ONa) + NaCl.$$

From our subsequent study of the ketyl compound, however, it is doubtful whether there is ever present any appreciable concentration of the disodio-compound (see following paper).

By means of this reaction several new dyes, not hitherto described because not readily obtainable by known methods, have been prepared. The yields are generally substantial; the carbinols

obtained have in some instances been difficult to purify, whilst in other instances good yields of the pure triarylcarbinol were readily obtained. The yield and quality of carbinol obtained vary with the reaction conditions and with the mobility of the reacting chlorine atom. As by-products, diaryls may be formed by the reaction $2RCl + 2Na = R{\cdot}R + 2NaCl$. On the other hand, the ketyl compound may undergo decomposition with formation of by-products, and may even react with toluene when this is used as solvent. The decomposition of the ketyl compound and its reactions will be discussed in Part II (following paper).

Attempts have been made to obtain dye-bases by heating the ketyl compounds with many other benzenoid chloro-compounds. The presence of groups which may be attacked by sodium, such as nitro- and amino-groups, is always inimical to the reaction. Dichloro-compounds, such as *p*-dichlorobenzene and 4 : 4′-dichlorodiphenyl, gave dye-bases, but difficulty was experienced in purifying them; whilst more highly chlorinated compounds, such as tetrachlorotoluene, only gave traces of dye-base, under the conditions used.

In purifying some of the carbinols obtained, it was observed that, when the dye salts were basified with ammonia, the basified product had an abnormally high nitrogen content. It was eventually proved that basification with ammonia gave, not the carbinol, but the corresponding amine, *e.g.*, $C(NH_2)(C_6H_4{\cdot}NMe_2)_2(C_6H_4Me)$. A similar observation has been made by Noelting and Saas (*Ber.*, 1913, **46**, 953), who obtained the amine $C(NH_2)(C_6H_4{\cdot}NMe_2)_3$ by the action of ammonia on an aqueous solution of crystal violet.

Experimental.

pp′-Tetramethyldiaminodiphenyl-o-tolylcarbinol, $[(CH_3)_2N{\cdot}C_6H_4]_2C(OH){\cdot}C_6H_4{\cdot}CH_3$.—A mixture of 13·4 g. of *pp′*-tetramethyldiaminobenzophenone, 2·3 g. of sodium, 7 g. of *o*-chlorotoluene, and 50 c.c. of dry toluene was heated in a closed flask provided with a stirrer at 100—105° for 16 hours. The ketone dissolved to a pale yellow solution, but as the reaction proceeded the mixture darkened and a light brown, crystalline powder gradually separated. A little water was added to the reaction mixture, and the toluene and any excess of *o*-chlorotoluene were removed by steam-distillation. The brown, gummy residue of impure carbinol became semi-solid on standing. From the aqueous liquor, a small quantity of *p*-dimethylaminobenzoic acid was obtained by neutralisation with acetic acid. The crude carbinol was extracted with ligroin, filtered from insoluble residue, and the solution evaporated. The carbinol so obtained was dissolved in 100 c.c. of boiling 10% oxalic acid solution and filtered from in-

soluble matter. The oxalate separated on cooling in green, bronzy crystals. These were redissolved in 100 c.c. of hot water and a further amount of insoluble matter was filtered off. This latter contained a little unchanged Michler's ketone. The residue left when the crude carbinol was extracted with ligroin consisted mainly of a product crystallising from toluene in colourless needles, m. p. 190°, which has been identified as *pp'*-tetramethyldiaminodiphenylbenzylcarbinol, $[(CH_3)_2N\cdot C_6H_4]_2C(OH)\cdot CH_2\cdot C_6H_5$. The mode of formation and properties of this substance will be discussed in Part II. The solution of the oxalate of the carbinol was basified with excess of sodium hydroxide. The blue precipitate of pp'-*tetramethyldiaminodiphenyl*-o-*tolylcarbinol* was filtered, washed, dried, boiled out with ligroin, and recrystallised from alcohol. It forms small colourless needles, m. p. 132·5°, becoming light blue on exposure to air. Yield, 8 g. (Found : N, 7·8. $C_{24}H_{28}N_2O$ requires N, 7·8%). The carbinol is moderately soluble in the cold in the usual organic solvents, and readily soluble in warm alcohol and toluene.

When the oxalate is basified with ammonia, pp'-*tetramethyldiaminodiphenyl*-o-*tolylmethylamine* is obtained, which, when recrystallised from ligroin–toluene, has m. p. 163° (Found : N, 11·7. $C_{24}H_{29}N_3$ requires N, 11·7%).

In concentrated sulphuric or hydrochloric acid, the carbinol gives a reddish-brown solution which turns green on addition of water, finally changing to blue. The oxalate gives an intense blue solution in water and a greenish-blue solution in alcohol. Aqueous solutions of the salts of the carbinol dye tannin-mordanted cotton greenish-blue.

Reduction of the carbinol with zinc and 2*N*-hydrochloric acid gave *pp'*-tetramethyldiaminodiphenyl-*o*-tolylmethane, white, glistening needles from alcohol, m. p. 102° (compare Noelting and Gerlinger, *Ber.*, 1906, **39**, 2042).

4-Chloro-*m*-xylene condenses similarly with Michler's ketone to give pp'-*tetramethyldiaminodiphenyl*-m-4-*xylylcarbinol*. This base crystallises from alcohol in small, colourless needles, m. p. 145°.

pp'-*Tetramethyldiaminodiphenyl*-p-*anisylcarbinol*,

$$(NMe_2\cdot C_6H_4)_2C(OH)\cdot C_6H_4\cdot OMe.$$

—A mixture of 13·4 g. of Michler's ketone, 2·3 g. of sodium, 7·5 g. of *p*-chloroanisole, and 50 c.c. of toluene was heated in a boiling water-bath for 12—16 hours in a closed flask with a stirrer. The crude carbinol, obtained by treating the product with water and removing toluene by steam-distillation, was converted into the *oxalate*, which crystallised in bronzy nodules. These were redissolved in hot water, filtered from a little ketone, and the solution was basified with ammonia; the bluish-white *carbinol* was filtered off, washed with a little alcohol, and dried. It separated from ligroin partly as

gum and partly as crystals; yield, 5·8 g. The latter crystallised from benzene–ligroin in almost colourless needles, m. p. 153° (Found: C, 76·6; H, 7·4; N, 7·5. $C_{24}H_{28}O_2N_2$ requires C, 76·6; H, 7·4; N, 7·4%). The carbinol dissolves in organic acids, *e.g.*, oxalic and acetic acids, to give intense green solutions. Mineral acids give brown solutions turning green on dilution with water. Solutions of the salts dye tannin-mordanted cotton greenish-blue.

pp′-*Tetramethyldiaminodiphenyl*-β-*naphthylcarbinol*.—A mixture of 6·7 g. of Michler's ketone, 1·2 g. of sodium, 4·5 g. of β-chloronaphthalene, and 30 c.c. of dry toluene was stirred for 4½ hours in a boiling water-bath. A dark-coloured product separated during the heating, and on cooling, a copious, grey, crystalline deposit was obtained. This was filtered, washed with a little toluene, and warmed with water; the crude carbinol then remained as a yellow, crystalline powder. The main impurities are unchanged ketone, β-chloronaphthalene, and an appreciable amount of ββ-dinaphthyl. The crude carbinol was purified by conversion into the crystalline oxalate and basification with ammonia; yield, 4·1 g. The *carbinol* crystallises best from aqueous pyridine (in needles) or from benzene–ligroin (in prisms), m. p. 181° (Found: N, 7·0. $C_{27}H_{28}N_2O$ requires N, 7·1%).

pp′-*Tetraethyldiaminodiphenyl*-β-*naphthylcarbinol*.—The reaction proceeds similarly with equivalent amounts of tetraethyldiaminobenzophenone, β-chloronaphthalene, and sodium. In this case the carbinol is easy to purify owing to its sparing solubility in hot alcohol, the impurities being readily soluble. The alcohol-extracted *carbinol*, recrystallised from benzene–ligroin, forms colourless plates, m. p. 177° (Found: N, 6·2. $C_{31}H_{36}N_2O$ requires N, 6·2%). Yield, 51%. The carbinol forms green salts with acids, and aqueous solutions of such salts dye tannin-mordanted cotton a bright yellowish-green.

pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylcarbinol*.—This carbinol is obtained when α-chloronaphthalene is heated with Michler's ketone and sodium. Owing to the greater reactivity of the α-chlorine atom, a much larger proportion of αα-dinaphthyl is formed and this product collects in the portion insoluble in oxalic acid. The crude carbinol is best purified by solution in hot toluene and partial precipitation with ligroin. pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylcarbinol* crystallises from acetone in colourless needles, m. p. 167° (Found: N, 7·0. $C_{27}H_{28}N_2O$ requires N, 7·1%). pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylmethylamine*, obtained by basifying the oxalate with ammonia, has m. p. 186° (Found: N, 10·3. $C_{28}H_{29}N_3$ requires N, 10·6%).

[illegible], MANCHESTER. [*Received, June 8th*, 1927.]

CCXCI.—*Reactions of Sodium Compounds of Aromatic Ketones. Part II. Their Reaction with Methyl and Methylene Groups and their Products of Decomposition.*

By Ernest Harry Rodd and Frank William Linch.

In the preceding paper, it was shown that Michler's ketone and its ethyl homologue combine with sodium in an indifferent solvent to form ketyl compounds which react with aryl chlorides to form triarylcarbinols. Further examination of these ketyl compounds has shown that they are remarkably reactive and that by their means syntheses of a hitherto unrecorded type can be effected. In the course of experiments on the action of sodium on Michler's ketone in toluene solution, a product was obtained in considerable quantity which was eventually proved to be *pp'*-tetramethyldiaminodiphenylbenzylcarbinol, and could only have been produced by the action of the ketyl compound on the methyl group of the toluene. This compound was found to be identical with that obtained as a by-product in the preparation of a triarylcarbinol from Michler's ketone and *o*-chlorotoluene by the action of sodium in toluene solution (Part I). Further experiments showed that the ketyl compound readily reacts with methyl and methylene groups which are generally only attacked by powerful oxidising agents. By this reaction we have been able to prepare with facility a number of new compounds which would be obtainable by known methods only with considerable difficulty.

The Reaction between Michler's Ketone and Toluene in the Presence of Sodium.—It has been shown by previous workers (see Part I) that benzophenone and other aromatic ketones form disodio-compounds, $CR_2(ONa)Na$. If a similar compound were formed by Michler's ketone, it should give, when decomposed by water, Michler's hydrol (tetramethyldiaminobenzhydrol). We attempted to prepare the hydrol by heating Michler's ketone in toluene solution with two atomic proportions of sodium, and obtained, besides the expected hydrol and other by-products which will be discussed later, a considerable yield of pp'-*tetramethyldiaminodiphenylbenzylcarbinol* (I). When benzene was used as solvent instead of toluene, no trace of this compound was formed.

The evidence for the constitution of the compound is as follows. Analysis indicated the formula $C_{24}H_{28}ON_2$, and a molecular-weight determination in camphor gave 350 (calc., 360). The compound shows the properties of a colour base, giving deep blue solutions when dissolved in dilute mineral or acetic acids, but when the solution is

heated the colour disappears. This colour change is due to the formation of a new base having the composition $C_{24}H_{26}N_2$, which has been identified as *ββ-tetramethyldiaminodiphenylstyrene* (II), m. p. 135°. The new base is evidently formed from the first by the loss of the elements of water, and since salt formation first occurs, the formation of the styrene may be represented thus:

$$CH_2Ph\cdot C(OH)\!<\!\begin{matrix}C_6H_4\cdot NMe_2\\C_6H_4\cdot NMe_2\end{matrix} \xrightarrow{HCl} CH_2Ph\cdot C\!<\!\begin{matrix}C_6H_4\cdot NMe_2Cl\\C_6H_4\cdot NMe_2\end{matrix}$$

(I.) (Blue.)

$$\xrightarrow{\text{on heating}} CHPh{:}C\!<\!\begin{matrix}C_6H_4\cdot NMe_2,HCl\\C_6H_4\cdot NMe_2\end{matrix} \text{ (II.)}$$

(Colourless.)

By oxidation of the tetramethyldiaminodiphenylbenzylcarbinol with lead peroxide in dilute hydrochloric acid in the cold, phenylacetic acid is obtained, whilst oxidation of the styrene compound readily gives first a greenish-blue dyestuff and then benzaldehyde. The styrene compound is stable to boiling alcoholic potassium hydroxide, but when fused with potassium hydroxide it gives Michler's ketone. All these reactions confirm the constitutions assigned to the two new bases.

The conversion of the carbinol into the styrene derivative is best effected by boiling it for a short time with 10% hydrochloric acid; when the solution is cooled the styrene separates as a sparingly soluble, white, crystalline *dihydrochloride*. This property facilitates the detection of the carbinol and the purification of the styrene. The dihydrochloride is hydrolysed by water with precipitation of the base. A characteristic property of this styrene, and of other similar compounds which we have made, is its oxidation in acetic or dilute mineral acid to an intense blue dyestuff by chromic acid or lead peroxide. The fact that solutions of the carbinol prepared in the cold do not give this reaction but that they give it after heating shows that the conversion of the carbinol into the styrene does not proceed readily in the cold. The cold oxidation of the carbinol to phenylacetic acid illustrates the same point.

When the identity of the product obained from toluene had been established, experiments were extended, and it was found that *p*-xylene gave a similar product with Michler's ketone, whilst tetraethyldiaminobenzophenone reacted similarly with toluene in the presence of sodium.

Reaction with Substances containing the Methylene Group.—Regarding the formation of a benzyl derivative from toluene as due to oxidation of the methyl group with simultaneous formation of benzhydrol, we considered that a substance containing a readily oxidisable methylene group should also react with the sodium

derivative of Michler's ketone. As a convenient substance with which to experiment we chose *pp'*-tetramethyldiaminodiphenylmethane. When this was heated with Michler's ketone and sodium in benzene solution, we obtained without difficulty a good yield of *octamethyltetra-aminotetraphenylethanol*,

$$(NMe_2 \cdot C_6H_4)_2C(OH) \cdot CH(C_6H_4 \cdot NMe_2)_2 \text{ (III)},$$

which by dehydration with sulphuric acid gave octamethyltetra-aminotetraphenylethylene, which has been described by Gattermann (*Ber.*, 1895, **28**, 2876) and Willstätter and Goldmann (*Ber.*, 1906, **39**, 3765). This observation confirmed our conclusions with regard to the reaction products from toluene, and suggested that the reaction might be of general application. To obtain further confirmatory evidence, carbinols were prepared from (*a*) Michler's ketone and tetraethyldiaminodiphenylmethane, and (*b*) tetraethyldiaminobenzophenone and tetramethyldiaminodiphenylmethane, and the two carbinols, $(NMe_2 \cdot C_6H_4)_2C(OH) \cdot CH(C_6H_4 \cdot NEt_2)_2$ (IV) and $(NEt_2 \cdot C_6H_4)_2C(OH) \cdot CH(C_6H_4 \cdot NMe_2)_2$ (V) were shown to give the same ethylene compound by dehydration with sulphuric acid.

Other substances of diverse character containing the methylene group, which have been found to react with the ketyl compound, are acenaphthene and fluorene. In each case, the expected compound was obtained without difficulty in benzene solution. Tetrahydronaphthalene, however, failed to react.

Decomposition Products of the Sodium Ketyl Compound and the Mechanism of its Reaction with Methyl and Methylene Groups.— To explain the ready attack of the ketyl compound on methyl and methylene groups, it is simplest to assume that the radicals $CR_2(ONa)\cdot$ (where $R = NMe_2 \cdot C_6H_4$) are the active agents. Since Michler's hydrol is always a product, the reaction, in the case of toluene, assumes the form $2CR_2(ONa)\cdot + CH_3Ph = CR_2H(ONa) + CR_2(ONa) \cdot CH_2Ph$. For this reaction, only one atom of sodium should be required per mol. of ketone, but when only one atomic proportion of sodium was heated with the ketone in toluene solution, although in the course of 2 hours the whole of the sodium had disappeared, yet no benzyl compound was formed. This observation led us to make a more careful study of the reaction.

With 0·95 atomic proportion of sodium, in two experiments, after heating in a closed vessel for 2 hours and 16 hours, respectively, identical results were obtained: no benzyl carbinol was found, about one-third of the ketone was recovered, and the products included about 0·1 mol. of Michler's hydrol, 0·2 mol. of dimethylaminobenzoic acid, and other bases, including much crystal violet. These, together with dimethylaniline, are the usual products under similar conditions.

When the sodium is increased to 1·5 atomic proportions, a maximum yield of benzylcarbinol is obtained, and sodium remains unchanged at the end; no ketone is recovered. The same result is obtained by using 2 atomic proportions of sodium. A typical experiment, with 1 mol. of Michler's ketone, gave approximately 0·37 mol. of tetramethyldiaminodiphenylbenzylcarbinol, 0·30 mol. of hydrol, 0·08 mol. of dimethylaminobenzoic acid, and 0·11 mol. of colour base.

When benzene is used as solvent, with 2 atoms of sodium, the principal product is Michler's hydrol, with a fair amount of colour base.

During the reaction, the solution gradually assumes an intensely greenish-blue colour, but if air is passed through the apparatus, no blue colour is produced, no hydrol is obtained, and most of the ketone is recovered unchanged, but some dimethylaminobenzoic acid and crystal violet are formed, together with a much redder dyestuff, probably indicating oxidation of the dimethylamino-groups of crystal violet.

If a chloro-compound is added to the reaction mixture, when only one atomic proportion of sodium or less is used, no blue colour appears, but the formation of dye base proceeds at once (*e.g.*, of malachite green, from chlorobenzene), and only traces of the above by-products are formed.

Whilst we feel that more data are required before an entirely satisfactory explanation can be given of all the above observations, we put forward the following discussion tentatively. First, with regard to the colour of the solution obtained when sodium dissolves in a solution of the ketone, it has been freely assumed by Schlenk that free radicals of the type $R_2C(ONa)\cdot$ are coloured, just as Gomberg assumes that free radicals, $R_3C\cdot$, have colour. If this assumption be accepted, then free radicals must always be present in our toluene solutions of the ketyl compound at all stages of the reaction, but the quantity of free radical present may be very small, since traces of oxygen rapidly decolorise the solution. In the presence of a chloro-compound, no colour ever appears, and since the formation of a triarylcarbinol starts at once, it is probably the monosodio-derivative of the ketone which attacks the chloro-compound, as suggested by Schlenk and Weickel to explain the action between sodiobis-diphenylyl ketone and methyl iodide (*Ber.*, 1911, **44**, 1182):

$$2R_2C(ONa)\cdot + R'Cl \begin{cases} \rightarrow R_2R'C(ONa) \xrightarrow{H_2O} R_2R'C(OH) \\ \rightarrow R_2CCl(ONa) \longrightarrow R_2CO + NaCl \end{cases}$$

It is not necessary then to assume the formation of a disodio-compound of the ketone (compare Part I).

The non-formation of benzyl compound when only one atom of sodium is used may be due to the greater tendency of a monosodio-radical to combine with another mol. of ketone than to attack a methyl group. We suggest that an intermediate compound, probably of the type $R_2C(ONa)\cdot O\cdot CR_2Na$, is formed,* combination taking place through the oxygen atom, rather than between two carbon atoms. It has been shown recently by Schorigen (*Ber.*, 1926, **59**, 2510) that when sodium acts on complex ethers the point of attack is the oxygen atom. Hence, when more than one atomic proportion of sodium is available, the intermediate compound would be attacked with formation of active free radicals which would attack the toluene :

$$\begin{array}{l} R_2C(ONa)-\!\!\!-\!\!\!-O \\ +\ C_6H_5\cdot CH_2-\!\!\!-H\ \ CR_2Na \end{array} + Na \longrightarrow \begin{array}{l} R_2C\!-\!\!-ONa \\ C_6H_5\cdot CH_2 \end{array} + \begin{array}{l} ONa \\ HCR_2 \end{array} + Na$$

It would appear that the additional sodium acts catalytically, and this agrees with the experimental results, as far as we can interpret them. Owing to side reactions, however, it has not been possible to determine how much of the sodium employed takes part in this reaction.

The observation that oxygen destroys the blue colour formed by the addition of sodium to the ketone, mainly with re-formation of the ketone, agrees with Schlenk's observations on simple aromatic ketones (*Ber.*, 1914, **47**, 487) :

$$2R_2C(ONa)\cdot + O_2 \longrightarrow R_2C(ONa)\cdot O\cdot O\cdot CR_2(ONa) \longrightarrow 2R_2C{:}O + Na_2O_2.$$

The formation of *p*-dimethylaminobenzoic acid, crystal-violet base, and dimethylaniline as by-products must be attributed to a general loosening of the bonds between the aryl radicals and the keto-carbon atom in the ketyl compound. Since these products are formed to the greatest extent when there is a deficiency of sodium, they are probably the result of internal rearrangement in a complex molecule or radical, *e.g.*, $CR_2(ONa)\cdot O\cdot CR_2\cdot \longrightarrow \cdot CR(ONa)\cdot O\cdot CR_3$ $\xrightarrow{+R_2CO}$ $R_2CNa\cdot O\cdot CR(ONa)\cdot O\cdot CR_3$. The last complex on hydrolysis should give 1 mol. each of Michler's hydrol, dimethylaminobenzoic acid, and crystal-violet base. Undoubtedly we have not yet identified all the by-products, so it is not possible to give a complete picture of the changes taking place. We do not exclude the possibility of the formation of the pinacol, $R_2C(ONa)\cdot CR_2(ONa)$, but we have as yet no evidence for it.

* This type of intermediate compound was also suggested by Beckmann and Paul (*Annalen*, 1891, **266**, 1) to explain the formation of benzophenone and benzhydrol from the monosodio-derivative of benzophenone.

EXPERIMENTAL.

The Michler's ketone used for these experiments was the technical product, purified by boiling with very dilute hydrochloric acid and recrystallising the insoluble portion from alcohol. The toluene used was the commercial product, redistilled and dried over sodium.

pp'-*Tetramethyldiaminodiphenylbenzylcarbinol* (I).—In a flask fitted with a sealed stirrer and a reflux condenser were placed 800 c.c. of toluene, 268 g. of Michler's ketone and 46 g. of sodium, and the whole was heated in a bath kept at 100—105° for 12 hours, with continuous stirring. During the heating, the colour of the solution became deep greenish-blue and remained so throughout the experiment. The blue colour is destroyed at once by air. The contents of the flask were cooled, poured off from the unchanged sodium, and treated with ice to hydrolyse the sodium compounds. The whole was then steam-distilled to remove the toluene and dimethylaniline, if any. The bases were filtered from the alkaline aqueous liquor and extracted thoroughly with ether. The residue consisted of nearly pure pp'-*tetramethyldiaminodiphenylbenzylcarbinol*, 131 g., m. p. 185°. (In those experiments in which only 0·95 mol. of sodium is used, the residue at this stage consists of nearly pure unchanged ketone, which is also almost insoluble in ether.) A similar experiment gave 36 g., m. p. 187°, from 67 g. of Michler's ketone. By recrystallisation from toluene the base is obtained in colourless, transparent needles, often pointed at one end only, m. p. 190·5° (Found: C, 79·62; H, 7·79; N, 7·72; *M*, cryoscopic in camphor, 350. $C_{24}H_{28}ON_2$ requires C, 80·00; H, 7·77; N, 7·77%; *M*, 360). The carbinol dissolves in acetic acid with a blue colour, which becomes intense on warming, then quickly fainter, and finally very pale blue.

The other products of the reaction were separated as follows: The alkaline filtrate obtained above was neutralised to precipitate the *p*-dimethylaminobenzoic acid, which was filtered, dried, and weighed. From the solid residue, consisting of carbinol and other bases, the ether had extracted the latter (see above), and this extract was freed from solvent and dissolved in dilute sulphuric acid. A strong solution of sodium hydrogen sulphite was then added, and the mixture warmed at 60°, whereby the Michler's hydrol was converted into *pp'*-tetramethyldiaminodiphenylmethane-ω-sulphonic acid. The solution was made alkaline with sodium hydroxide, filtered from the precipitated bases, and the sodium ω-sulphonate salted out (when dried, it is approx. 80% pure). The bases were extracted with dilute oxalic acid solution (which left a little ketone in those cases where there was a deficiency of sodium, see p. 2181) and the solution

yielded a considerable amount of crystal violet oxalate. Other bases (unidentified) were, however, also present.

In one experiment, the dimethylaniline in the recovered toluene was found to be 1·4 g. from 67·0 g. of ketone, and the other products, separated as described above, were 27·0 g. of the benzylcarbinol (m. p. 190°, crude), 5·0 g. of dimethylaminobenzoic acid, about 26 g. of Michler's hydrol, and 8·5 g. of crude crystal-violet base.

An experiment was carried out in which the apparatus was sealed with special care and connected to a manometer, after the required temperature had been attained. There was no evidence of any change of pressure, showing that no gaseous products are formed.

ββ-pp′-*Tetramethyldiaminodiphenylstyrene* (II).—This may be prepared from the crude *pp′*-tetramethyldiaminodiphenylbenzylcarbinol by dissolving 20 g. in 100 c.c. of 2*N*-hydrochloric acid and boiling for ½ hour; on cooling, the solution deposits 20 g. of the *dihydrochloride* of the styrene in soft, shining, colourless needles (Found in crude product: Cl, 16·0. $C_{24}H_{28}N_2Cl_2$ requires Cl, 17·1%). The basification is carried out by suspending the hydrochloride in water and gradually stirring in dilute sodium hydroxide. The *base*, recrystallised from a mixture of acetone and methyl alcohol, forms short, pale yellow prisms, m. p. 135° (Found: C, 84·66, 84·21; H, 7·90, 7·92; N, 8·17. $C_{24}H_{26}N_2$ requires C, 84·21; H, 7·60; N, 8·19%). In a quantitative experiment on the conversion of the pure benzylcarbinol into the styrene, 0·7662 g. of the former gave 0·7250 g. of the latter (theory, 0·728 g.).

Oxidation of pp′-*Tetramethyldiaminodiphenylbenzylcarbinol.*—14·4 G. of the carbinol were dissolved in 350 c.c. of cold *N*-hydrochloric acid. A thin paste of 29 g. of lead peroxide was added gradually to the stirred solution of the carbinol and oxidation was allowed to proceed for some hours at the ordinary temperature. The lead was precipitated with sodium sulphate and the filtrate basified with sodium hydroxide. The alkaline solution was extracted with ether, but the basic products of the oxidation could not be obtained sufficiently pure for identification. The solution was then acidified with dilute hydrochloric acid and again extracted with ether. After removal of the ether, an oily residue was left which solidified on standing (5·1 g.). It was recrystallised twice from hot water, giving large, glistening plates, m. p. 76—77°. This product had all the properties of phenylacetic acid, and its identity was established by comparison (mixed m. p.) with a sample prepared from benzyl cyanide.

Octamethyltetra-aminotetraphenylethanol, (III).—A mixture of 26·8 g. of Michler's ketone, 4·6 g. of sodium, 50 g. of *pp′*-tetramethyldiaminodiphenylmethane, and 100 c.c. of dry benzene was heated

at 85—90° for 16 hours with efficient stirring. The sodium was separated and the benzene removed by steam-distillation. The residual white solid was filtered off and boiled out twice with alcohol to remove Michler's hydrol and other impurities. The insoluble white residue (20 g.) was substantially pure *octamethyltetra-aminotetraphenylethanol*. It is sparingly soluble in all neutral organic solvents and is best recrystallised from toluene; colourless needles, m. p. 255° (Found: C, 77·7; H, 8·0; N, 10·7. $C_{34}H_{42}N_4O$ requires C, 78·1; H, 8·0; N, 10·7%). It dissolves in weak mineral acids or glacial acetic acid to give greenish-blue salts which become violet on addition of lead peroxide.

The same method of preparation and the same molecular proportions of materials were used in the following preparations.

αα-4 : 4′-*Tetraethyldiaminodiphenyl*-ββ-4 : 4′-*tetramethyldiaminodiphenylethan-α-ol* (V) from *pp′*-tetraethyldiaminobenzophenone and *pp′*-tetramethyldiaminodiphenylmethane: white needles from toluene or alcohol–chloroform, m. p. 228° (Found: N, 9·6. $C_{38}H_{50}N_4O$ requires N, 9·7%).

αα-4 : 4′-*Tetramethyldiaminodiphenyl*-ββ-4 : 4′-*tetraethyldiaminodiphenylethan-α-ol* (IV) from *pp′*-tetramethyldiaminobenzophenone and *pp′*-tetraethyldiaminodiphenylmethane: white needles from toluene or alcohol–chloroform, m. p. 229—230° (Found: N, 9·6. $C_{38}H_{50}N_4O$ requires N, 9·7%).

Both compounds dissolve in dilute mineral acids or glacial acetic acid, giving greenish-blue solutions which turn violet on the addition of a little lead peroxide. These ethanol derivatives were converted into the corresponding ethylene compounds by warming with concentrated sulphuric acid.

Octamethyltetra-aminotetraphenylethylene,

$$(NMe_2{\cdot}C_6H_4)_2C{:}C(C_6H_4{\cdot}NMe_2)_2.$$

—5 G. of the ethanol were dissolved in 25 c.c. of concentrated sulphuric acid and warmed for ½ hour in a boiling water-bath. The pale green solution was poured into ice water and the base precipitated by the addition of sodium hydroxide as a yellowish-white powder; yield 4·7 g. It crystallises from acetone–methyl alcohol in greenish-yellow needles, m. p. 314—316° (Gattermann, *Ber.*, 1895, **28**, 2876, gives m. p. 310—315°) (Found: N, 11·1. Calc. for $C_{34}H_{40}N_4$: N, 11·1%). It forms colourless salts when dissolved in acids, but the solutions turn violet on the addition of a little lead peroxide.

αα-4 : 4′-Tetraethyldiaminodiphenyl-ββ-4 : 4′-tetramethyldiaminodiphenylethanol and αα-4 : 4′-tetramethyldiaminodiphenyl-ββ-4 : 4′-tetraethyldiaminodiphenylethanol when warmed with concentrated sulphuric acid gave the same product, *viz.*, αα-4 : 4′-*tetraethyldiaminodiphenyl*-ββ-4 : 4′-*tetramethyldiaminodiphenylethylene*, pale

yellow needles from alcohol–chloroform, m. p. 212°. The identity was established by mixed melting-point and nitrogen determinations (Found: N, 10·0, in each case. $C_{38}H_{48}N_4$ requires N, 10·0%).

4 : 4′-*Tetramethyldiaminodiphenylacenaphthenylcarbinol*, $(NMe_2{\cdot}C_6H_4)_2C(OH){\cdot}C_{12}H_9$.—A well-agitated mixture of 26·8 g. of Michler's ketone, 4·6 g. of sodium, 30 g. of acenaphthene, and 100 c.c. of dry benzene was heated at 85—90° for 16 hours. The excess of sodium was separated and the benzene removed by steam-distillation. The residual crystalline mass was filtered off and boiled several times with alcohol to remove impurities. The white, insoluble residue (12 g.) was recrystallised from toluene; colourless needles, m. p. 232° (Found: N, 6·7. $C_{29}H_{30}ON_2$ requires N, 6·6%). It dissolves in dilute mineral acids or glacial acetic acid to reddish-blue solutions. These solutions are almost decolorised by boiling, and on the addition of a little lead peroxide the resulting solution assumes a violet colour.

4 : 4′-*Tetramethyldiaminodiphenylmethyleneacenaphthene*, $(NMe_2{\cdot}C_6H_4)_2C{:}C_{12}H_8$.—Since concentrated sulphuric acid sulphonates the acenaphthene nucleus, in this case the ethylene derivative was prepared by boiling 5 g. of the ethanol for an hour with aqueous hydrochloric acid. On cooling, a crystalline *hydrochloride* was deposited in fine, white needles. The *base* was obtained as a greenish-yellow powder by basifying with sodium hydroxide. The dried product (4·7 g.) was recrystallised from chloroform–alcohol; pale yellow plates, m. p. 209° (Found: N, 7·0. $C_{29}H_{28}N_2$ requires N, 6·9%). It dissolves in acetic acid to a colourless solution which turns violet on addition of lead peroxide.

4 : 4′-*Tetramethyldiaminodiphenylmethylenefluorene*, $[N(CH_3)_2{\cdot}C_6H_4]_2C{:}C\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$.—A mixture of 13·4 g. of Michler's ketone, 2·3 g. of sodium, 20 g. of fluorene, and 50 c.c. of dry benzene was heated with stirring at 85—90° for 16 hours. The unchanged sodium (0·5 g.) was separated and the benzene removed by steam distillation. The residual, orange, crystalline product was boiled three times with alcohol and the insoluble residue (8·5 g.) was recrystallised first from toluene and finally from chloroform–alcohol; pale yellow needles, m. p. 239—240° (Found: N, 6·7. $C_{30}H_{28}N_2$ requires N, 6·7%). It dissolves in dilute mineral acids or acetic acid to a pale yellowish-green solution which turns blue on addition of lead peroxide. In this case, dehydration of the carbinol to the ethylene derivative has occurred at some stage which has not been determined.

The analyses recorded in Parts I and II were carried out by Mr. W. H. Cliffe, whose help we gratefully acknowledge. The work was carried out in the Research Department of the British Dyestuffs Corporation, Ltd., to whom our thanks are due for permission to publish it.

BLACKLEY, MANCHESTER. [*Received, June 8th*, 1927.]

Addendum.—Since the above work was completed, a paper by Madelung and Völker has appeared (*J. pr. Chem.*, 1927, **115**, 24), in which the formation of *pp'*-tetramethyldiaminodiphenylbenzylcarbinol and of *pp'*-tetramethyldiaminodiphenylstyrene from Michler's ketone and magnesium benzyl chloride is described, the styrene being the principal product. The m. p.'s are stated to be 173° and 129°, respectively, whereas our m. p.'s are 190·5° and 135°. The above authors' compounds are evidently impure, and are most probably contaminated with unchanged ketone, since our observations have shown that with Michler's ketone the Grignard reaction only proceeds to a very limited extent. It is to be noted that earlier workers, by the action of magnesium alkyl halides on Michler's ketone, never obtained carbinols, but always the corresponding ethylene derivative. Madelung and Völker state that the carbinol and the styrene both give the same blue colour in acetic acid (*loc. cit.*, pp. 29, 41). This does not agree with our observations; we find that the former gives a very intense blue colour with cold acetic or with one equiv. of dilute mineral acid, comparable in intensity with the colour given by a true triphenylmethane-dye base, whilst the styrene gives a very weak colour. When the intensely coloured solution of the carbinol in acid is heated, the colour gradually disappears and finally approximates in intensity to that given by the styrene.

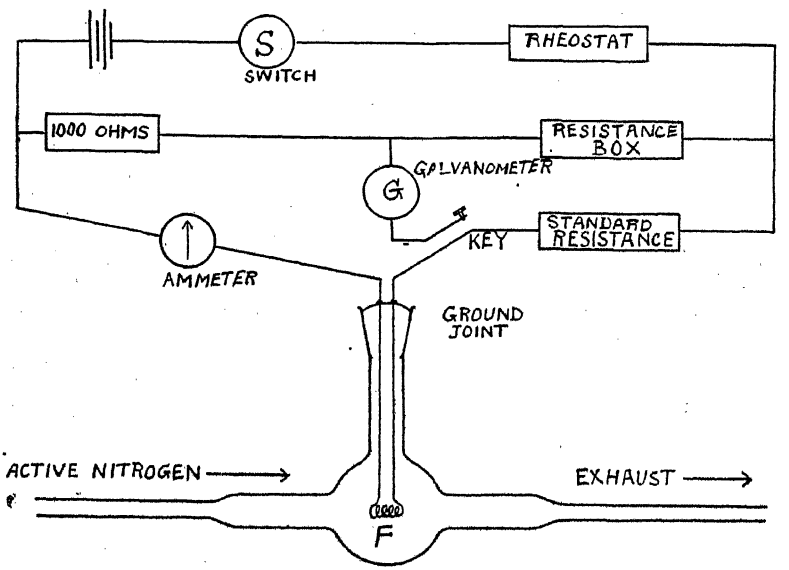
CCXCII.—*On Active Nitrogen. Part III. Active Nitrogen and the Metals.*

By ERIC JOHN BAXTER WILLEY.

WHILST metallic vapours readily combine with active nitrogen to form nitrides (Rayleigh, *Proc. Roy. Soc.*, 1913, *A*, **88**, 539; Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 263), the clean, cold metals rarely exert any noticeable influence upon the afterglow. In ordinary circumstances, copper forms the only exception to this statement, but if mercury or low-melting alloys of lead be employed and the gas be bubbled through the liquid, this rapidly becomes foul and abundant nitride formation occurs, suggesting that the inactivity

of the clean and cold metals is due to the formation of a skin of nitride, which, being inactive, protects the underlying portions of the metal against attack. In view of the fundamental importance of nitride formation in the catalysts employed in the synthesis of ammonia, it was decided to investigate in some detail the effect of active nitrogen on the metals; the results obtained support the foregoing theory, and, moreover, it has been found that in several cases the metals become active catalysts in the destruction of the afterglow at the temperature of decomposition of their nitrides. The experimental data also show that the energy of active nitrogen

FIG. 1.



is *ca.* 45,000 cals./g.-mol., in excellent agreement with the value advanced in earlier communications (J., 1926, 1804; this vol., p. 669), and that the decay process is probably bimolecular with respect to the active nitrogen.

EXPERIMENTAL.

The apparatus employed is shown in Fig. 1. Active nitrogen, cooled to room temperature by passage down a thin-walled tube, flowed over the filament, F, which served both as a resistance thermometer and as a heating coil. The galvanometer and leads were enclosed in an earthed shield, and an auxiliary electrode, also earthed, was provided between F and the end of the discharge tube

order to afford protection from stray discharges; in this way, disturbance of the Wheatstone circuit was avoided. The filament was silver-soldered to heavy copper leads sealed through the ground joint as shown.

It was found that both with a bare platinum filament initially at room temperature and with filaments of other metals, as well as those obtained by electrodeposition of coatings so thin as not appreciably to alter the resistance of the original platinum, a very definite increase in temperature occurred when active nitrogen was drawn through the apparatus; this was least in the case of molybdenum and tungsten, and greatest with smooth-surface copper. No such increase in temperature was observed when the filament was replaced by a thermometer, thus showing that the heating effect is due to the decay of the endothermic active nitrogen at the surface of the metal.

With platinum, iron, silver, zinc, tungsten, and molybdenum, the relationship between the velocity of the gas stream (measured upon an arbitrary scale) and filament temperature was linear between the limits examined. The figures obtained for platinum are typical:

Flow speed	0·0	4·0	6·5	8·5	10·3	12·3
Resistance	1·302	1·313	1·320	1·325	1·330	1·335

(Owing to the limited capacity of the pump, it was not possible to work with flow speeds above 1·5 litres/hour, measured at atmospheric pressure.)

With a copper-coated filament, however, the temperature increment was much greater than that obtained previously and the glow ceased abruptly at the metallic surface; moreover, the curve obtained (Fig. 2) is different in form, the temperature rapidly increasing to a value at which it remains constant over a certain range of flow rate, and then again increasing. The existence of this flat portion, AB, is explicable on the assumption that the maximum destruction of active nitrogen at the surface is reached with a gas-velocity corresponding to the ordinate of A, but that at B the gas-velocity is high enough to set up turbulent motion round the filament, causing increased circulation of the gas and a consequent increase in the number of molecules deactivated by the metal. Support for this view was obtained in two ways. It was noticed that so long as the gas-velocity was not too high, the coating of copper remained intact and the experiments could be repeated as often as desired. Above a gas-velocity corresponding closely with B, however, the point at which the afterglow ceased (initially about 2 m. downstream in such experiments) began to recede rapidly, until after about a minute no afterglow was visible except

for localised patches round the electrodes. When the filament was dismounted, the copper coating was found to have vanished almost entirely, whilst the walls of the bulb had become reddish-brown in colour, just as if they had been " spattered " from a copper cathode. Prolonged treatment of the glass with nitric acid produced no change in its colour, and little or no copper could be detected in solution; but quantitative tests in which a long filament was first plated with copper and then cut in two, one half being used for a colorimetric determination of the copper and the other being subjected to the action of active nitrogen, showed that nearly the whole of the copper lost from the wire could be recovered from the bulb if this were powdered and fused with sodium carbonate. Even with the most rigorous protection against stray discharges, the result was the same, and hence it would appear that the disintegration is due to the evolution of heat at the copper surface owing to the decay of large amounts of active nitrogen thereat, whilst the scattered metal has so strong a catalytic effect as to " poison " the glass.

The nature of the copper surface has a great influence in this connexion. If the plating is spongy, the curve obtained shows only the merest trace of flattening, and the disintegration is rapid even at lower gas velocities than before. This " spattering " effect was still more pronounced when the coating had been prepared *in situ* by the reduction of copper oxide by means of active hydrogen in an auxiliary apparatus, whilst commercial copper wire which had been carefully cleaned did not show it at all. No other metal showed any disintegration.

It seems probable, therefore, that, in the case of other metals, the linear relation between gas-velocity and filament temperature corresponds with the portion of the curve to the left of A (Fig. 2), and that if a sufficiently high flow speed could have been attained, they would have given curves showing a similar flattening. It is possible, upon the basis of the data obtained here, to calculate (i) the relative order of catalytic efficiencies of these metals for the destruction of active nitrogen, and (ii), provided a certain assumption be made, the order of the decay process of active nitrogen.

(i) All other factors remaining constant, the increase in the temperature (ΔT) of a filament will be directly proportional to its area (A) and to the catalytic efficiency of the metal (E), and inversely proportional to its weight (W), *i.e.*, $\Delta T = kAE/W$. Now it was noticed that when a current of active nitrogen was drawn past a copper-coated filament, the glow appeared to be entirely extinguished provided that the flow speed was not too high, and hence we may assume that in these circumstances the whole of the

active nitrogen reaching the surface of the filament was transformed to the inert variety. We may thus calculate the catalytic efficiencies of the various metals employed, relative to copper as unity, as shown in Table I. The measurements were all made with filaments immersed in nitrogen flowing at the rate of 1·5 litres/hr. (measured at *N.T.P.*), the gas being at a pressure of 10 mm. Hg and containing 1·5% of active nitrogen.

TABLE I.

Metal.	100 *W*.	ΔT.	$A \times 10^4$.	*E*.
Platinum	0·85	8·0	2·2	0·24
Silver	2·1	12·5	3·9	0·26
Zinc	2·1	12·5	3·9	0·26
Iron	2·0	13·0	3·7	0·27
Copper (smooth)	1·15	36·0	2·8	1·00
Copper (spongy)	1·84	15·0	3·6	0·33
Tungsten	2·3	0·0	—	0·0
Molybdenum	0·8	0·0	—	0·0

(ii) Let us make the very probable assumption that a constant fraction of the active nitrogen present at any instant is decomposed at the filament surface; then, from the linear relation between the flow speed and the temperature increment in the filament, we see that the number of active nitrogen molecules present at any instant varies directly with the flow speed of the gas and therefore inversely as the time (t) taken for a molecule to travel from the discharge to the filament, *i.e.*,

$$[N_2'] = k'/t, \text{ or } -d[N_2']/dt = k'/t^2.$$

Hence the decay process is, upon this assumption, bimolecular with respect to the active nitrogen.

It was hoped to use the results of these experiments in conjunction with the Hertz–Knudsen equation (which provides a means of calculating the number of molecular impacts per unit area per second) to evaluate the energy of active nitrogen. Such attempts, however, did not lead to intelligible results. It was then thought that if the "blanketing" effect of the converted nitrogen round the filament could be eliminated by the use of a hot wire, data of more value might be obtained, for it is obvious that the conditions obtaining near the cold filaments are somewhat complicated. Furthermore, the metals should, *ex hypothesi*, become completely active at or about the temperatures of decomposition of their nitrides, and this view was tested in the next series of experiments.

The temperature of the wire was gradually raised by altering the adjustment of the rheostat, and its resistance was determined for each setting in a stream of inert nitrogen at 10 mm. pressure, a constant flow speed being maintained all the time; the usual

parabolic relationship between current and resistance was obtained, as shown in Figs. 3 A, B, and C. The nitrogen was then activated and the procedure repeated, with the result that in the case of

FIG. 2.

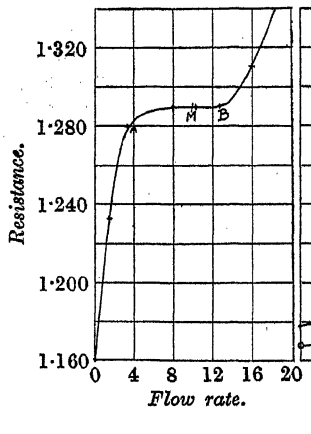
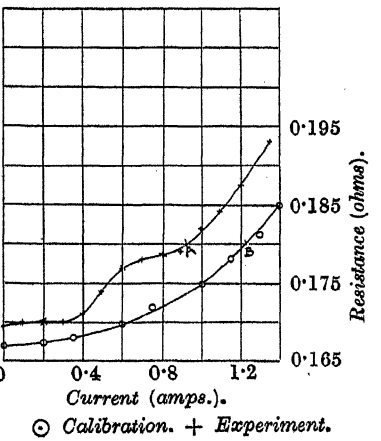
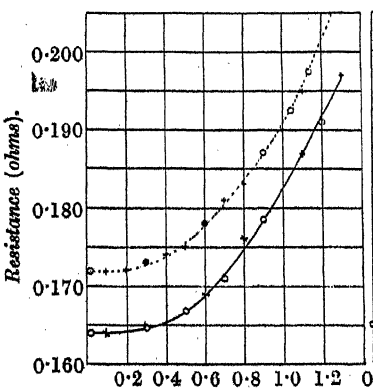


FIG. 3A.
Silver.



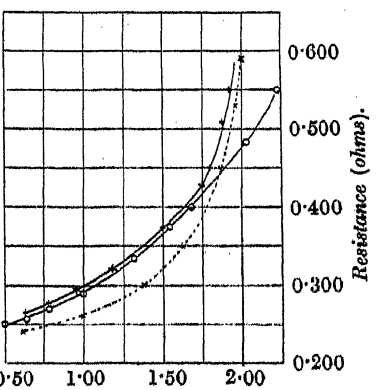
⊙ *Calibration.* + *Experiment.*

FIG. 3B.
Copper.



Calibration ———
Experiment – – – –
\+ *Current increasing.*
⊙ „ *decreasing.*

FIG. 3C.
Iron.



⊕ *Calibration.*
\+ *Expt. current increasing.*
× „ „ *decreasing.*

iron (Fig. 3 C), platinum, and silver (Fig. 3 A) marked "breaks" were found in the curves, at *ca.* 300°, 92°, and 30°, respectively. Moreover, at these temperatures the glow practically ceased as the

active nitrogen reached the filament, indicating that it was being destroyed by the hot wire. No departure from the calibration curve was noticed with tungsten and molybdenum filaments, but with copper (Fig. 3 B) the form of the curve shows that the section above the break has already been reached even at the ordinary temperature.

It will be noticed that, in the case of the iron-coated filament, the curves obtained for increasing and decreasing values of the current do not coincide; it is possible that this is due to sintering, in view of the temperature to which the filament was raised, for when the original deposit was replaced by a fresh one the discontinuity occurred just as before. No formation of nitride was observed in any of these experiments, but the platinum filament became coated with a dense layer of platinum-black, as observed by Beilby and Henderson (J., 1901, **79**, 1253) when this metal was heated in a current of gaseous ammonia.

Since it seemed likely that the comparative inactivity of commercially drawn copper wire as a catalyst for the decay of active nitrogen is due to surface phenomena which might be minimised when a hot filament is in contact with active nitrogen, the ordinary material was used in this case, with the result, as will now be shown, that complete activity appeared when the hot metal was used. The significance of these breaks in the curves is clearly that at the temperature concerned the filament is becoming catalytically active in the destruction of active nitrogen; energy is therefore being liberated and the rise in temperature of the filament follows. From these data we may evaluate approximately the energy of active nitrogen, as follows.

Consider two points, A and B, on a line parallel to the abscissa (in Fig. 3 A) which is drawn to cut the two curves where they have become approximately parallel. Then the energy supplied by the active nitrogen (in cals./sec.) is

$$R_T(C^2_B - C^2_A)/4{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where R_T is the ohmic resistance of the filament at the points A and B, and C_A and C_B are the currents (amps.) corresponding to A and B, respectively.

Since at this point the glow had almost entirely been lost in the gas below the filament, we may assume that all the active nitrogen passing was destroyed, and from a knowledge of the flow rate of the gas and its active-nitrogen content we can calculate n, the number of molecules undergoing conversion per second. Thus from (i) we have $R_T(C^2_B - C^2_A) = nq$, where q is the energy of a single

molecule of active nitrogen. The energy of active nitrogen per g.-mol., Q, is then given by the expression :

$$Q = R_T(C^2_B - C^2_A) \times 6{\cdot}06 \times 10^{23}/4{\cdot}2n.$$

TABLE II.

Metal.	R_T.	C_A.	C_B.	Flow speed (c.c./hr. at $N.T.P.$)	$n \times 10^{-17}$.	Q.
Platinum ...	0·530	0·45	0·54	1500	1·7	40,200
Silver	0·180	0·92	1·24	3000	3·4	52,700
Copper	0·175	0·48	0·80	2000	2·2	47,000
					Mean	46,600

It will be noticed that if evaluations of Q are made from the two curves just after activity has set in, values much higher than 46,000 cals./g.-mol. are obtained. This is probably due to the "blanketing" effect mentioned on p. 2192, and it was therefore necessary to make calculations from points on the curves corresponding to a sufficiently high temperature to ensure an adequate circulation of the gas, *i.e.*, from points at which the curves are parallel.

It now remains to discuss the probable mode of action of the metals upon active nitrogen. The existence of definite points at which they became active (and in two cases, a definite action of the active nitrogen upon the metal surface) would point to the catalytic decay process being due to the alternate formation and decomposition of the nitride, and the temperatures in question lend a certain measure of support to this view. This is most apparent in the case of iron, since the activity sets in at about 300° and the nitride commences to decompose between 300° and 400° (Baur and Voerman, *Z. physikal. Chem.*, 1905, **52**, 467; White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343; Noyes and Smith, *ibid.*, 1921, **43**, 475). The temperatures of decomposition of the corresponding substituted-ammonia compounds of silver, platinum, and copper do not appear to have been determined, although the data of Beilby and Henderson (*loc. cit.*) show that they are comparatively low, and in the absence of evidence to the contrary we may regard this tentative explanation as justified.

Summary.

The catalytic activity of certain metals in the form of fine filaments in accelerating the decay of active nitrogen has been studied both at the ordinary and at higher temperatures. From the data obtained an evaluation of the energy of active nitrogen has been made which agrees well with the value already found, and it appears

that the activity of the metals in this respect probably depends upon the stability of their nitrides; of the metals employed, copper appears to be by far the most active. It has also been shown that the decay process of active nitrogen in the gas phase is bimolecular with respect to the active nitrogen.

The author's acknowledgments are due to Dr. E. K. Rideal for his interest and advice with regard to these experiments.

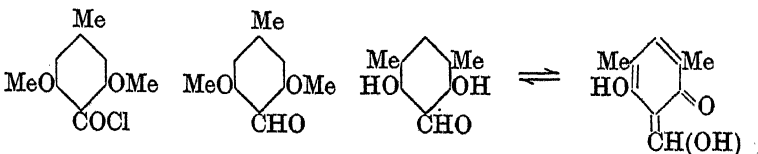
LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE.
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CCXCIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XIV.*

By ALEXANDER ROBERTSON and ROBERT ROBINSON.

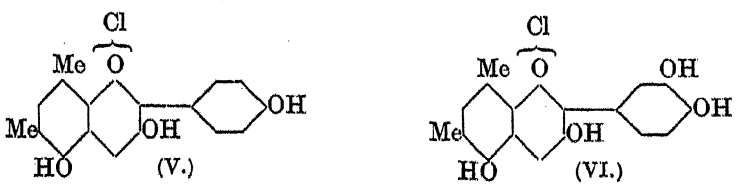
ALL the anthocyanins derived from cyanidin chloride (3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride) which have been described by Willstätter and his collaborators give a strong ferric chloride reaction, and hence the attachment of the sugar residues to positions 3′ and 4′ is highly improbable. Moreover, we know that the free hydroxyl-group combination (3 : 7 : 3′ : 4′) leads to the exhibition of an alkali colour-reaction practically identical with that due to the combination (3 : 5 : 7 : 3′ : 4′), whilst, on the other hand, the combination (5 : 7 : 3′ : 4′) produces a different effect. The evidence would clearly be much more complete if the effect of the combination (3 : 5 : 3′ : 4′) could be estimated, and the present communication includes a description of flavylium salts containing free hydroxyl groups in these positions. The results may be stated as follows. The combination (3 : 5 : 3′ : 4′) is intermediate between (3 : 7 : 3′ : 4′) and (5 : 7 : 3′ : 4′), and whilst it is closer to the former in one substance, it is closer to the latter in another; thus the influences of small constitutive variations are sufficiently pronounced to diminish the value of the argument from the colour-reactions. The present results are, however, in complete agreement with the conclusions of Pratt and Robinson (J., 1925, **127**, 1131) regarding the constitution of the anthocyanins. In order to obtain 3 : 5 : 3′ : 4′-tetrahydroxyflavylium salts by the usual methods, we required 2 : 6-dihydroxybenzaldehyde or a suitable derivative. The first line of attack was through *p*-orsellinic acid, the method for the preparation of which has been greatly improved. The acid could not be reduced directly by means of sodium amalgam in the presence of boric acid and *p*-toluidine (or sodium bisulphite), although Weil

(*Ber.*, 1922, **55**, 224, 301, 2664) has applied this process with satisfactory results to the reduction of derivatives of salicylic acid. Next, 2 : 6-*dimethoxy*-4-*methylbenzoyl chloride* (I) could not be reduced directly by Rosenmund's method, neither could the *imino-chloride* derived from the related p-*toluidide* be reduced by following the conditions prescribed by Sonn in analogous cases (*Ber.*, 1919, **52**, 1927). The *nitrile* corresponding to (I) could, however, be reduced by an application of the method due to Stephen (J., 1925, **127**, 1874), although the aldehyde (II) was obtained in poor yield and was found to be useless for the special purpose in view. Finally, we succeeded in obtaining a substituted 2 : 6-dihydroxybenzaldehyde, namely, m-*xylorcylaldehyde* (III), by applying the Gattermann synthesis to *m*-xylorcin. The aldehyde is a bright yellow substance, and for this reason it may be best represented by the constitution (IV).



(I.) (II.) (III.) (IV.)

On condensation with ω : 4-dimethoxyacetophenone and ω-methoxyacetoveratrone in formic acid solution under the influence of hydrogen chloride, the *m*-xylorcylaldehyde readily yielded *flavylium* salts which, after demethylation, had the formulæ (V) and (VI), respectively.

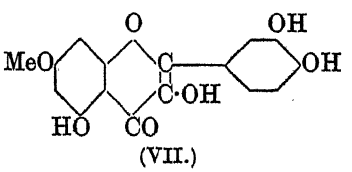


(V.) (VI.)

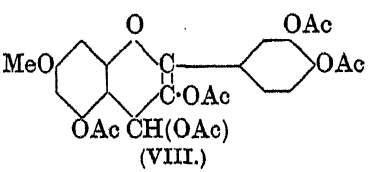
The reactions of (V), taken in conjunction with other similar data, suggest that pelargonin is a pelargonidin 5-diglucoside and callistephin a pelargonidin 3-glucoside, but in view of the problematic effect of the methyl groups, the 7-saccharide configuration is not definitely excluded in either case. The alkali colour-reaction of (VI) is similar to that exhibited by mecocyanin, but the methyl groups may have a reddening influence, as indeed the properties of rhamnetinidin (see below) suggest. A survey of commercial dyestuffs provides no certain guide as to the probable effect on the colour of the substitution of methyl for hydrogen. Thus new magenta is bluer than magenta, but phenosafranine is bluer than

safranine-T, and further conflicting cases could be quoted. In order to obtain a flavylium salt with free hydroxyl groups in the positions 3 : 5 : 3′ : 4′, still more closely related to a cyanidin 7-glucoside, we have reduced the flavonol rhamnetin (VII) to the related *rhamnetinidin chloride* (IX). Rhamnetin is known to be quercetin 7-methyl ether because on fission it yields phloroglucinol monomethyl ether, and on methylation quercetin 3 : 7 : 3′ 4′-tetramethyl ether, the so-called yellow quercetin tetramethyl ether. The specimen employed was derived from xanthorhamnin and was free from quercetin and rhamnazin. The reduction of quercetin to cyanidin chloride was accomplished by Willstätter and Mallison (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769), who employed magnesium as the reducing agent in methyl-alcoholic hydrogen chloride solution; the yield was poor and the product was difficult to isolate. We made many unsuccessful experiments with the object of improving the direct method, and therefore had to resort to an indirect process.

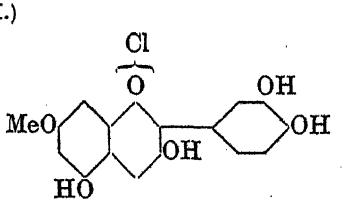
Rhamnetin was acetylated and reduced by zinc dust in boiling acetic anhydride solution (Herzig's acetylating reduction). The product [probably containing (VIII)] was then hydrolysed by means of aqueous-alcoholic hydrochloric acid with formation of rhamnetinidin chloride and other substances. This method constitutes an advance, although the yield of pure product remains unsatisfactory. The insoluble by-products probably arise from a pinacol



(VII.)



(VIII.)



(IX.)

formed in the reduction, and the optimum conditions for the process are being studied in detail in connexion with the reduction of quercetin and kaempferol. The alkali colour-reaction of rhamnetinidin is much closer to that of cyanidin and cyanin than to that of mecocyanin. This is the most definite evidence at our disposal, and it points clearly to the conclusion that mecocyanin, chrysanthenin, asterin, idaein, keracyanin, and prunicyanin are cyanidin 3-saccharides. Similarly, cyanin is indicated as a cyanidin 5-diglucoside,

but we are on less safe ground here, since it is the general experience that purification of an anthocyanidin makes the alkali colour-reaction become bluer and never redder. Whilst, therefore, the fact that rhamnetinidin surpasses mecocyanin in the purity (absence of red) of the blue colour of its alkaline solutions could hardly be explained away as due to impurity of the rhamnetinidin (the presence of cyanidin in significant amount being excluded by the determination of methoxyl content and by the ascertained absence of quercetin in the rhamnetin employed), yet we could not, in view of the circumstances, be sure that further purification would not yield a rhamnetinidin having reactions identical with those of cyanin and cyanidin.

EXPERIMENTAL.

p-Orsellinic Acid and some Derivatives.—The method adopted for the preparation of the acid is based on that by means of which Brunner (*Annalen*, 1907, **357**, 321) obtained γ-resorcylic acid in 40% yield from resorcinol. A mixture of orcinol (20 g.), potassium bicarbonate (40 g.), and glycerol (40 g.) was heated (oil-bath at 115—120°) for 6 hours in an atmosphere of carbon dioxide. The *p*-orsellinic acid (16 g.) isolated from the reaction product is almost pure and, after crystallisation from boiling water (some decomposition to orcinol) and drying at 100°, had m. p. 165—166° (decomp.). The methyl ester has previously been obtained by Herzig (*Monatsh.*, 1903, **24**, 894) by the action of diazomethane on the acid. We have prepared the substance by the action of methyl iodide on silver *p*-orsellinate in boiling benzene solution. It crystallises from light petroleum in elongated, flat prisms, m. p. 93—94° (Herzig gives m. p. 98—99°) (Found: C, 59·4; H, 5·7. Calc. for $C_9H_{10}O_4$: C, 59·4; H, 5·5%). The m. p. could not be raised by repeated crystallisation. The ethyl ester has previously been obtained by Lipp and Schiller (*Ber.*, 1909, **42**, 1967) as a by-product from the condensation of ethyl sodioacetoacetate and propylene dibromide. These authors quote the m. p. 61°; we applied the silver-salt method and our ester crystallised from 60% alcohol in prismatic needles, m. p. 62°. These esters, like *p*-orsellinic acid, give a blue coloration with ferric chloride. [The publication of Wagenhofer on the complete methylation of *p*-orsellinic acid (*Monatsh.*, 1924, **45**, 223) appeared in the course of our work.] The acid (15 g.) was methylated by means of methyl sulphate (58 g.) and aqueous sodium hydroxide, giving methyl *p*-orsellinate dimethyl ether (12 g.). This ester has m. p. 86°, and on hydrolysis yields the acid, m. p. 180—182° (decomp.) (Found: C, 61·5; H, 6·3. Calc. for $C_{10}H_{12}O_4$: C, 61·3; H, 6·1%) (Herzig, *loc. cit.*, gives m. p. 178°).

2 : 4-*Dimethoxy*-6-*methylbenzaldehyde* (*Orcylaldehyde Dimethyl Ether*).—This substance, stated to melt at 62°, has been prepared by Gattermann by nuclear synthesis from orcinol dimethyl ether (*Annalen*, 1907, **357**, 372). We prepared the compound from orcylaldehyde in order to carry out certain confirmations of orientation, and because we were attempting the synthesis of the isomeric *p*-orcylaldehyde dimethyl ether. The methylation of the aldehyde (1 mol.) was effected by means of methyl sulphate (1·5 mol.) and aqueous sodium hydroxide (2 mol.). The alkali-insoluble product crystallised from light petroleum in small, colourless needles, m. p. 64—65°. On oxidation with potassium permanganate, orsellinic acid dimethyl ether was obtained in good yield. This crystallised from 20% acetic acid in glistening prisms, m. p. 143—144° (decomp.) (Found : C, 61·2; H, 6·2. Calc. for $C_{10}H_{12}O_4$: C, 61·3; H, 6·1%). The acid (m. p. given as 140°) has been previously obtained by Herzig (*loc. cit.*) by hydrolysis of the product of methylation of orsellinic acid by diazomethane. A mixture of the dimethyl ethers of orsellinic acid and *p*-orsellinic acid began to melt at 130°.

2 : 6-*Dimethoxy*-4-*methylbenz*-p-*toluidide*.—Phosphorus pentachloride (9 g.) was added to a mixture of *p*-orsellinic acid methyl ether (8 g.) and carbon tetrachloride (or benzene) (50 c.c.), and the reaction completed at 50°. The residue, left after the removal of the solvent and phosphoryl chloride under diminished pressure, was redissolved in benzene (100 c.c.) which was distilled away as before, leaving the 2 : 6-*dimethoxy*-4-*methylbenzoyl chloride* (I) as a mass of colourless needles, m. p. 84—85° (for the purest specimen obtained). The p-*toluidide* was obtained by the action of an excess of *p*-toluidine on a solution of the acid chloride in benzene. It crystallised from benzene, followed by light petroleum, in colourless needles, m. p. 168—169° (Found, in material heated at 100° for 6 hours with loss of benzene : C, 71·7; H, 6·8. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·6%). This *p*-toluidide is moderately readily soluble in methyl or ethyl alcohol, and sparingly soluble in benzene or light petroleum. From a suspension of it in benzene (6 g. in 50 c.c.) the corresponding *imino-chloride* was prepared by the action of phosphorus pentachloride (5 g.) for 10 minutes on the steam-bath. After removal of the benzene and phosphoryl chloride, a colourless solid was obtained. On exposure to moist air, this was quickly converted into the original *p*-toluidide, m. p. 168—169°.

2 : 6-*Dimethoxy*-4-*methylbenzamide*, $(MeO)_2C_6H_2Me{\cdot}CO{\cdot}NH_2$.—A stream of ammonia was led through a solution of 2 : 6-dimethoxy-4-methylbenzoyl chloride (10 g.) in benzene (150 c.c.), and the solid which separated was collected, washed with water, and crystallised

from benzene; slender needles, m. p. 199° (yield, 7 g.) (Found: C, 61·5; H, 6·8. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%). Its solubilities resemble those of the *p*-toluidide.

2 : 6-*Dimethoxy*-4-*methylbenzonitrile*.—A solution of the foregoing amide in pure thionyl chloride was boiled for 5 minutes, and the thionyl chloride then distilled under diminished pressure; the last traces were eliminated by the addition of benzene and redistillation. The *nitrile* (yield, 65—70%) crystallises from benzene–light petroleum in prismatic rods, m. p. 138—139° (Found: C, 68·0; H, 6·5. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2%). The substance may also be crystallised from 60% alcohol in large, squat prisms.

2 : 6-*Dimethoxy*-4-*methylbenzaldehyde* (II).—Hydrogen chloride was led into a mixture of powdered anhydrous stannous chloride (15 g.) and ether (150 c.c.) until a homogeneous solution was obtained. 2 : 6-Dimethoxy-4-methylbenzonitrile (6 g.), dissolved in a little chloroform, was then added, and the passage of hydrogen chloride continued until the liquid was saturated. Crystals separated after 12 hours; after 14 days, the separated solid weighed 8 g. and ultimately about 1 g. more was obtained. This double tin salt crystallised in needles and was very difficult to hydrolyse. The best results were obtained by dissolution in water at 40—50°, addition of an excess of sodium acetate, and heating on the steam-bath for 3 minutes. The *aldehyde* (1·5 g.) was isolated by means of ether, and crystallised from light petroleum in long, colourless, prismatic needles, m. p. 90—91° (mixed m. p. with orcylaldehyde dimethyl ether, 50—55°) (Found: C, 66·7; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). This substance is readily soluble in ether and the simple alcohols, moderately readily soluble in benzene, and slightly soluble in hot water. It yields a yellow, sparingly soluble p-*nitrophenylhydrazone* and reduces an ammoniacal silver solution. All attempts to condense it with ω-methoxyacetoveratrone were fruitless, and, no doubt as the result of steric hindrance, it does not appear to form a Schiff's base by condensation with aniline.

4-*Nitro*-6-*hydroxy*-m-*xylene*.—The nitration of *m*-xylidine (100 g.) by the method of Nöelting and Collins (*Ber.*, 1884, **17**, 265) gave 4-nitro-6-amino-*m*-xylene (80 g.), and this was converted into the corresponding phenol by the following method (compare D.R.-PP. 95,339 and 97,012) which is superior to that described by Pfaff (*Ber.*, 1883, **16**, 616). A diazonium salt solution, prepared at below 0° from the nitro-amine (16·6 g.), sulphuric acid (50 g.), crushed ice and water (300—350 g.), and sodium nitrite (7 g.), was filtered and gradually added to boiling 55% sulphuric acid (350 c.c.). On cooling, the nitroxylenol separated in light brown crystals (12—

14 g.), which could be employed for the next stage. The substance crystallised from hydrochloric acid in very slender needles, m. p. 95°. The reduction to 4-amino-6-hydroxy-*m*-xylene (Pfaff, *Ber.*, 1883, **16**, 1137) was conveniently effected by means of iron in alcoholic solution (compare West, J., 1925, **127**, 494). Iron powder (80 g.) was added in portions of about 10 g. at intervals of 3 minutes to a boiling solution of the nitro-*m*-xylenol (55 g.) in alcohol (300 c.c.) and concentrated hydrochloric acid (20 c.c.), and the mixture was boiled for 5 hours, a test then showing that reduction was complete. The filtered solution was concentrated to 100 c.c., cooled, and saturated with hydrogen chloride. After keeping in an ice-chest for some hours, the hydrochloride was collected, and a further quantity could be isolated from the mother-liquor by concentration to 50 c.c. and renewed saturation with hydrogen chloride. The salt crystallised in glistening plates; total yield of practically pure substance, 45 g.

m-*Xylorcin*.—The method of Pfaff (*loc. cit.*) for the preparation of this phenol gave unsatisfactory results, and we adopted the following procedure: 4-Amino-6-hydroxy-*m*-xylene hydrochloride (16 g.) was dissolved in 10% sulphuric acid (200 c.c.) by heating, and crushed ice (200 g.) was added after sudden cooling and shaking to ensure the separation of small crystals. Sodium nitrite (6·4 g.), dissolved in a little water, was then introduced, and the mixture stirred until the sulphate had disappeared. A little charcoal was added, and the diazo-solution filtered and gradually added to 600 c.c. of boiling 10% sulphuric acid. Very little tarry matter was produced, and the filtered solution (charcoal), which was almost colourless, was saturated with ammonium sulphate. Part of the xylorcin crystallised and was collected; the remainder was isolated by six extractions with ether. The product crystallised from benzene in colourless, hexagonal plates, m. p. 124—125° (yield, 8—10 g.). The substance has the properties attributed to it by Pfaff.

m-*Xylorcylaldehyde* (III).—A mixture of *m*-xylorcin (10 g.), anhydrous hydrogen cyanide (15 c.c.), and ether (150 c.c.) was saturated with hydrogen chloride, and the aldimine-hydrochloride separated in almost colourless, prismatic needles in 1 hour. After keeping over-night, the salt was collected, washed with ether, dried, and dissolved in cold water (200 c.c.). The solution was heated at 80—90° for 15 minutes, and a part of the *aldehyde* crystallised, the remainder separating in long, yellow needles on cooling. The substance was recrystallised from 40% ethyl alcohol (charcoal); bright yellow, prismatic needles, m. p. 155—156° (Found: C, 64·8; H, 6·0. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). So far as we are able to judge, the striking colour of this substance is not due to

impurity, and Gattermann has noted the yellow colour of 4 : 8- and 2 : 7-dihydroxynaphthaldehyde (Annalen, 1907, **357**, 341).

3 : 4′-*Dimethoxyflavylium Chloride*.—Bright scarlet needles (changing to orange-red on contact with air) separated when hydrogen chloride was passed into a solution of salicylaldehyde (2·2 g.) and ω : 4-dimethoxyacetophenone (3·4 g.) in ether (80 c.c.). The *chloride* recrystallised from 8% hydrochloric acid in glistening, red, prismatic needles (yield, 5·7 g.) (Found, in material dried over sulphuric acid in a high vacuum for 12 hours : C, 60·0; H, 5·7. $C_{17}H_{15}O_3Cl,2H_2O$ requires C, 60·3; H, 5·6%). The substance is sparingly soluble in cold dilute hydrochloric acid, but easily soluble in the hot solvent. The ferrichloride crystallised from acetic acid in small, dull orange, prismatic needles, m. p. 151—152°. Pratt and Robinson described (J., 1923, **123**, 751) hair-fine, orange-red needles, m. p. 135°, so that it is possible that this substance exists in two modifications. The crystalline form, colour, and melting point are different, and in repeating the preparation through the unsaturated ketone we obtained the salt, m. p. 151—152°.

3 : 4′-*Dihydroxyflavylium Chloride*.—This salt is of interest inasmuch as it contains hydroxyl groups in the two positions considered to have the greatest effect on the alkali colour-reactions of the anthocyanidins. Thus, a comparison of the colour of alkaline solutions of this salt and of 7 : 3′ : 4′-trihydroxyflavylium chloride and the representative of the 5 : 3′ : 4′-hydroxylated series described below demonstrates the relatively feeble hypsochromic character of the hydroxyl groups in positions 7 and 5. A mixture of 3 : 4′-dimethoxyflavylium chloride (2·5 g.), phenol (10 g.), and hydriodic acid (60 c.c.; *d* 1·7) was boiled for 30 minutes in an atmosphere of carbon dioxide. After cooling, the phenolic layer was separated, and the demethylated *iodide* was obtained in slender, bright red needles by the addition of ether (yield, 0·7 g.). The *chloride*, obtained in the usual manner by means of silver chloride in methyl-alcoholic solution, was precipitated, after concentration, by dilute hydrochloric acid as a mass of bright red plates, and crystallised from 5—6% hydrochloric acid in red plates exhibiting a golden reflex. Rapid cooling causes the separation of needles (Found, in material dried over soda-lime for 12 hours : C, 59·6; H, 5·1.

$$C_{15}H_{11}O_3Cl,1{\cdot}5H_2O$$

requires C, 59·7; H, 4·7%). The salt crystallises from ethyl-alcoholic hydrogen chloride in flat, pointed prisms. It is moderately soluble in 4—6% hydrochloric acid and very readily soluble in hot dilute or concentrated hydrochloric acid, giving orange to orange-red solutions. When it is treated with much water, a colourless solution of the pseudo-base is obtained, addition of acids

restoring the orange-yellow colour of the flavylium salt. Aqueous or aqueous-alcoholic sodium carbonate dissolves the salt to a red solution, tinged with violet.

5-*Hydroxy*-3 : 4′-*dimethoxy*-6 : 8-*dimethylflavylium Chloride*.—A solution of *m*-xylorcylaldehyde (2 g.) and ω : 4-dimethoxyacetophenone (3 g.) in formic acid (25 c.c.) was saturated with hydrogen chloride, kept for 48 hours, and mixed with an excess of dry ether. The precipitated dark brown, prismatic needles were collected and crystallised from 8% hydrochloric acid as a dark brown, matted mass of slender, woolly needles (3 g.) (Found, in material dried over soda-lime for 12 hours : C, 57·1 ; H, 6·2. $C_{19}H_{19}O_4Cl,H_2O$ requires C, 57·4 ; H, 6·3%).

The *ferrichloride* crystallised from acetic acid in spherical aggregates of brown, prismatic needles, m. p. 211—212° after darkening at 190°.

3 : 5 : 4′-*Trihydroxy*-6 : 8-*dimethylflavylium Chloride* (V).—The foregoing dimethyl ether (2 g.) was demethylated by boiling hydriodic acid (60 c.c. ; *d* 1·7) and phenol (20 g.) in 40 minutes (passage of carbon dioxide). The iodide was precipitated from the separated phenolic layer by means of ether in purple rods (1 g.), and converted into the *chloride* in the usual way. This salt separated from its concentrated aqueous methyl-alcoholic hydrochloric acid solution in violet, prismatic needles, and was recrystallised from 8% hydrochloric acid ; glistening, violet needles (Found, in material dried in a high vacuum over sulphuric acid for 24 hours : C, 63·9 ; H, 5·1. $C_{17}H_{15}O_4Cl$ requires C, 64·1 ; H, 4·7%). This salt is very sparingly soluble in cold dilute hydrochloric acid but dissolves freely in the hot solvent to a reddish-brown solution. Unlike most flavylium salts, the anhydrous material is not hygroscopic and, as the crystals suffered no change in appearance on drying, it would appear that they separated in the anhydrous condition. The alcoholic solutions are not fluorescent, and on dilution with water give almost colourless solutions of the pseudo-base. The colour of the solution in aqueous sodium carbonate is reddish-violet, and in aqueous-alcoholic sodium carbonate, bluish-violet.

5-*Hydroxy*-3 : 3′ : 4′-*trimethoxy*-6 : 8-*dimethylflavylium Chloride*.—The condensation of *m*-xylorcylaldehyde and ω-methoxyacetoveratrone was carried out as in the analogous case (above) and the yield was almost quantitative. A hot solution of the crude salt in 0·5% hydrochloric acid was filtered, and the acid concentration increased to 8%. The dark red, woolly needles which separated were collected, and when dried exhibited a green reflex. The solutions in hot 7—8% hydrochloric acid are deep crimson, and on cooling, the separation of the salt is almost complete. The *ferri-*

chloride crystallised from acetic acid in reddish-brown, elongated, rhombic plates, exhibiting a bluish-green reflex; m. p. 200—203° (Found: C, 44·6; H, 3·9. $C_{20}H_{23}O_5Cl_4Fe$ requires C, 44·5; H, 3·9%). This derivative is readily soluble in hot acetic acid, and separates almost completely on cooling the solution.

3 : 5 : 3′ : 4′-*Tetrahydroxy*-6 : 8-*dimethylflavylium Chloride* (VI).—The chloride (1·5 g.) last described was demethylated under the usual conditions by hydriodic acid (80 c.c.; *d* 1·7) in presence of phenol (15 g.) in 30 minutes. Water (30 c.c.) was added, the phenolic layer separated, and the *iodide* precipitated by the addition of ether. The slender, red needles were collected and converted into the *chloride* by means of silver chloride in hot dilute hydrochloric acid solution. On standing, the cooled solution deposited dark red, microscopic, slender needles, and these were recrystallised from 10% hydrochloric acid (Found, in material dried in a high vacuum over sulphuric acid for 24 hours: C, 58·1; H, 5·1. $C_{17}H_{15}O_5Cl,H_2O$ requires C, 57·9; H, 4·8%). The salt is readily soluble in hot dilute hydrochloric acid, giving deep red solutions that deposit crystals but slowly on cooling. It dissolves in aqueous sodium carbonate to a bluish-violet solution, unchanged, in the absence of oxygen, by the addition of sodium hydroxide. In alcoholic solution, the sodium carbonate reaction is also violet, but this becomes blue on the addition of sodium hydroxide. The ferric chloride reaction in alcoholic solution is intense violet.

Rhamnetinidin Chloride (IX).—The crude rhamnetin obtained by hydrolysis of xanthorhamnin from Persian berries, was thoroughly extracted with boiling alcohol to remove quercetin, and then with hot acetic acid to remove rhamnazin. Finally it was purified through its monopotassium salt (Perkin and Wilson, J., 1903, **83**, 136). The light yellow product was dried at 140° (Found: MeO, 9·7. Calc.: MeO, 9·8%). A mixture of rhamnetin (4·6 g.), potassium acetate (5 g.), and acetic anhydride (80 c.c.) was boiled for 2—3 minutes (acetylation cannot be complete at this stage), and a large excess of zinc dust added in small portions in rapid succession. When further additions produced no change in the appearance of the solution (about 5 mins.), the liquid was boiled for 5 minutes longer, then cooled, decanted, and added to 500 c.c. of water containing concentrated hydrochloric acid (25 c.c.). The zinc was washed with a little acetic acid. The ochreous, sticky product was collected on a glass rod and on the sides of the container, washed with water, dissolved in alcohol (100 c.c.) and hydrochloric acid (30 c.c.), and the solution boiled for 20 minutes, the red colour of the flavylium salt appearing during this process. The crimson solution was concentrated in a vacuum, a little water being added

from time to time. When most of the colouring matter had been precipitated, the substance was collected, thoroughly extracted with a large volume of ether, and the residue with boiling 0·5% hydrochloric acid. The salt was precipitated from the filtrates, after concentration, by concentrated hydrochloric acid, and this operation was repeated. The product was then fractionally crystallised by slow evaporation of an alcoholic solution containing 10% hydrochloric acid; some tarry matter was first eliminated and then definite prismatic crystals separated. These were collected, twice recrystallised in the same way, and air-dried (Found: C, 51·9; H, 4·7; MeO, 8·3. $C_{16}H_{13}O_6Cl,2H_2O$ requires 51·6; H, 4·6; MeO, 8·6%). After this had been exposed to a vacuum for 12 hours, the analytical results indicated a monohydrate, but were not sufficiently sharp. *Rhamnetinidin chloride* is very sparingly soluble in cold 0·5% hydrochloric acid, readily soluble in the hot solvent to a brownish-red solution; the alcoholic solutions are bluish-red. The salt crystallises from aqueous-alcoholic hydrochloric acid in clusters of elongated prisms, orange-red by transmitted light, and forming a dark purplish-brown mass exhibiting an intense green reflex. On the addition of aqueous sodium carbonate to the solid salt, a blue solution is obtained. This is bluer than that of mecocyanin and redder than that of cyanidin, cyanin, or fisetinidin under the same conditions. Thick layers are violet-red, and this dichroism is the chief distinction from fisetinidin. On progressive dilution the colour becomes violet and finally blue. In alcoholic solution, the distinction from mecocyanin is much more pronounced, since with sodium carbonate under similar conditions, rhamnetinidin gives a blue solution (on the red side by comparison with cyanidin), whereas mecocyanin gives a violet solution. On the addition of sodium hydroxide to the alcoholic solution, mecocyanin and rhamnetinidin give identical pure blue colorations. The ferric chloride reaction of rhamnetinidin is blue in alcoholic solution and violet in aqueous solution.

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CCXCIV.—*A New Method of (Absolute) Potentiometric Titration.*

By BERNARD CAVANAGH.

THE following is an account of a new method of titration which combines great simplicity with the highest precision and with other special advantages. No potentiometer or standard cell is required, no normal electrode or reference "half-cell" and no mechanical stirrer, neither is any sort of liquid junction involved. Small quantities of solution can be rapidly titrated in an ordinary flask, with the aid only of a rheostat or resistance, a key, and a pointer-galvanometer. Yet the sensitivity and precision are the highest attainable by electrometric methods, and, in addition to its convenience for ordinary titrations, the method is especially suited for the titration of (*a*) very dilute solutions and (*b*) very small volumes (micro-titration).

This paper deals with the titration of the following ions: $H^{\cdot}$, $Ag^{\cdot}$, OH', Cl', Br', I'. The underlying principles will first be discussed.

1. The fundamental idea consists in the application to electrometric titration of the long-known principle of the Helmholtz cell, or cell without liquid junction. A familiar example of this type of cell is that consisting of a hydrogen electrode and either a calomel or a silver chloride electrode in one and the same solution of hydrochloric acid. The *E.M.F.* of this cell at the temperature T is given by

$$E = E_0 + 2RT/F \,.\, \log_e C\gamma,$$

where E_0 is a constant and C is the concentration of hydrochloric acid; or, if for the present we ignore the correction factor γ, *i.e.*, the "activity coefficient," and consider a particular temperature, *e.g.*, 16°, we may write

$$E = E_0 + 0{\cdot}1147 \log_{10} C \quad . \quad . \quad . \quad . \quad (1)$$

More generally, if for pure hydrochloric acid we substitute a mixed electrolyte containing hydrogen ions and chlorine ions at different concentrations, C_H and C_{Cl}, then the *E.M.F.* of the cell will be

$$E = E_0 + 0{\cdot}05735 \log (C_H \times C_{Cl}) \quad . \quad . \quad . \quad (2)$$

It is plain, therefore, that if we know E_0 and *one* of the factors C_H or C_{Cl}, we can determine the other by measuring E. This would be an example of what is commonly called a "physical" method of analysis.

Alternatively, we may gradually remove one of the ions from the solution by means of a standard reagent, the *residual* concentration

of the ion being, at each stage, indicated by the value of E, until that residual concentration either (*a*) can be neglected or (*b*) (for refined titration) reaches a certain value known to characterise the exact end-point of the titration. For instance, at the end-point in the titration of a chloride against silver, the value of C_{Cl} is equal to the solubility, S_{AgCl}, of silver chloride. The *E.M.F.* at the end-point would therefore be, in accordance with equation (2):

$$E = (E_0 + 0{\cdot}05735 \log S_{AgCl}) + 0{\cdot}05735 \log C_H \quad . \quad . \quad (3)$$

the bracketed expression being a known constant, so that the end-point *E.M.F.* depends on C_H, the acidity of the solution. A rough knowledge of C_H, however, is sufficient to permit high precision in the titration. Thus, even if C_H were estimated at *twice* its true value, the error produced in the end-point would be only $1{\cdot}5 \times 10^{-7}$ g.-equiv. per 10 c.c. of solution, which is only 1·5% in the titration of $N/1000$-solution, so that only when high precision in the most dilute solutions is required, will C_H have to be known more accurately.

Similarly, at the end-point in the titration of a strong acid by a strong base the value of C_H is equal to the acidity, h, of distilled water under the conditions prevailing. (The value of h depends ordinarily on the amount of carbon dioxide in the air and may be between 2×10^{-6} and 3×10^{-6}.) We obtain therefore a formula for the end-point potential of the same type as (3), *viz.*,

$$E = (E_0 + 0{\cdot}05735 \log h) + 0{\cdot}05735 \log C_{Cl} \quad . \quad . \quad (4)$$

so that in this case we need a rough knowledge of C_{Cl}.

It is plain that we have here a means of absolute * potentiometric titration in a single vessel without a liquid junction, and it may be observed that the resistance can thus easily be kept low, so that the method is peculiarly useful for the titration of dilute solutions without the employment of a refined galvanometer. It seems probable that the principle may be widely applicable.

2. *Elimination of the Potentiometer.*—The use of a potentiometer has been implied since we have to determine when the potential between the two electrodes reaches a certain end-point value. The instrument, it is true, need be only of simple pattern, and may be set for the end-point *E.M.F.*, so that the end of the titration is shown in practice by the reversal of the galvanometer deflexion; but we can eliminate the necessity for a potentiometer if we can

* The end-point is marked by the *E.M.F.* attaining a particular absolute value. This is the case also in the methods of Treadwell and of Müller. In all other methods, the end-point is marked by the attainment of a maximum value by the differential dE/dx, the rate of change of potential. It can be shown that the intrinsic sensitivity of the "absolute" methods is the higher.

construct a cell that will develop the required end-point *E.M.F.*, which might be done by imitating the composition which the titrated cell should have at the end-point. For instance, for the titration of a chloride, we might take a solution having the same acidity as the titrated solution, and shake it with some well-washed, precipitated silver chloride. A hydrogen electrode and a silver chloride electrode dipping into such a solution should develop the required end-point *E.M.F.* This procedure would bear the same relation to the (alternative) use of the potentiometer as the method of Treadwell bears to that of Müller.

A much simpler and more trustworthy procedure is available, however, for comparison of (1) and (3) shows that they become identical when $C^2 = S_{AgCl} \times C_H$; and it follows that if we take some hydrochloric acid of approximately the concentration C, where

$$C = \sqrt{S_{AgCl} \times C_H} = 0{\cdot}0031\sqrt{C_H} \quad . \quad . \quad . \quad (5)$$

(C_H being, as before, the acidity of the *titrated* solution), then a hydrogen and a silver chloride electrode dipped into this solution will develop the end-point *E.M.F.* This is more trustworthy than the other form of end-point cell because, the concentrations of both ions being considerable, there is less liability to polarisation during the titration. It follows from the relation (5) that, just as C_H need not be accurately known (see p. 2208), so C, the concentration of the hydrochloric acid in the end-point cell, does not require accurate adjustment.

In just the same way, for the titration of a strong acid by a strong base we obtain from (1) and (4) the relation $C^2 = hC_{Cl}$, and adopting $2{\cdot}5 \times 10^{-6}$ as a mean value for h (see p. 2208), we have

$$C = 0{\cdot}0016\sqrt{C_{Cl}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as the strength of the hydrochloric acid solution required, in terms of the chloride concentration. (In the total absence of carbon dioxide, the numerical coefficient would be 0·0003.)

3. *The Silver Chloride–Quinhydrone Cell.*—Of late, the hydrogen electrode has been superseded for many purposes by the more convenient " quinhydrone electrode," since Biilmann showed that, for solutions not distinctly alkaline, the presence of a trace of quinhydrone in solution caused a smooth platinum electrode to behave as a reversible hydrogen electrode.

It appeared possible that an exceedingly simple form of the Helmholtz cell might be obtained by merely dipping a smooth platinum electrode and a silver chloride electrode into a solution containing hydrogen ions, chlorine ions, and a little quinhydrone, providing always that the electrodes did not interfere with one another.

In the first experiments, a plain silver wire was used, in the presence of a visible precipitate of silver chloride, but the results were unsatisfactory owing possibly to some slight catalysis of the quinhydrone reaction on the metallic surface. When, however, the silver was coated electrolytically with silver chloride, excellent and quickly reproducible results were obtained.

Many measurements were made with cells containing various proportions and concentrations of the two ions, and the results, substituted in the more exact form of equation (2), *viz.*,

$$E = E_0 + 0{\cdot}05735 \log a_{\mathrm{H}} a_{\mathrm{Cl}} \quad . \quad . \quad . \quad . \quad (7)$$

(a_{H} and a_{Cl} being "corrected concentrations" or activities) gave the mean value 0·4740 for E_0. The measurements covered the whole range of the titrations of both ions, up to and beyond the end-points, leaving no doubt as to the practicability of using this very simple form of cell. In fact, the results were so uniformly good as to prompt an investigation, now in progress, of the suitability of this type of cell as a means of "physical" analysis.

4. *The Silver–Quinhydrone Cell and the Solubility of Silver Chloride.*—It is of interest that, *beyond* the end-point in the chloride titration, we have in effect the rather remarkable one-solution cell, Ag | Ag^+, H^+ (quinhydrone) | Pt, or, if we regard the quinhydrone electrode as a hydrogen electrode, Ag | Ag^+, H^+ | H_2, of which the *E.M.F.* is given by

$$E = E'_0 + RT/F \,.\, \log a_{\mathrm{Ag}}/a_{\mathrm{H}} \quad . \quad . \quad . \quad . \quad (8)$$

and is thus practically unaffected by the addition of water.

The results in this region were very good and yielded the value 0·1009 for E'_0. Now the activity-product of silver chloride, and hence its true solubility in pure water, S_{AgCl}, is readily obtained from E_0 and E'_0, for

$$-2RT/F \,.\, \log S_{\mathrm{AgCl}} = E_0 + E'_0 = 0{\cdot}5749 \text{ (at } 16°),$$

whence $S_{\mathrm{AgCl}} = 0{\cdot}97 \times 10^{-5}$ at 16°, with a probable accuracy of $\pm 2\%$.

5. *Final Simplification: Elimination of the End-point Cell.*—It is evident, therefore, that the method of titration outlined in Sections 1 and 2 is fully applicable with the more convenient silver chloride–quinhydrone cell. A final simplification of apparatus and procedure, however, now becomes possible, arising out of the value of E_0, given above.* Substituting 0·4740 for E_0 and $0{\cdot}97 \times 10^{-5}$ for

* This simplification is *not* available if the hydrogen electrode is used, because of the *negative* value of E_0 in that case.

S_{AgCl} in equation (3), we have, for the end-point potential in the titration of a chloride,

$$E_{Cl} = 0{\cdot}1866 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad . \quad (9)$$

this being the formula required when a potentiometer is used (see Section 12). Now calculation shows that E_{Cl} vanishes when $C_H = 5{\cdot}6 \times 10^{-4}$, *i.e.*, if the acidity of the solution is roughly $N/1800$, the end-point potential will be zero, and we require neither a potentiometer nor a second pair of electrodes to balance it. One pair of electrodes and a galvanometer is then all the physical apparatus required for the titration.

Similarly, for the acid–alkali titration, substituting for E_0 and for h in equation (4), we obtain for the end-point potential

$$E_H = 0{\cdot}153 + 0{\cdot}05735 \log C_{Cl} \quad . \quad . \quad . \quad . \quad (10)$$

which vanishes when $C_{Cl} = 2{\cdot}2 \times 10^{-3}$ (or $N/450$).

6. *The Bromide and the Iodide Cells.*—From similar series of measurements with the corresponding silver bromide (or iodide)–quinhydrone cells, the values 0·6235 and 0·8460, respectively, have been obtained for E_0, and $5{\cdot}6 \times 10^{-7}$ and $6{\cdot}5 \times 10^{-9}$ for the solubilities of the bromide and iodide. Hence we obtain for the end-point potentials:

$$E_{Br} = 0{\cdot}261 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad . \quad (11)$$
$$E_I = 0{\cdot}3725 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad (12)$$

which vanish, respectively, when $C_H = 2{\cdot}8 \times 10^{-5}$ or $3{\cdot}2 \times 10^{-7}$.

When the end-point cells are required in the titration of bromide and iodide, it is convenient still to use the hydrochloric acid cell, of which the *E.M.F.* is

$$E_{HCl} = 0{\cdot}4740 + 0{\cdot}1147 \log C \quad . \quad . \quad . \quad . \quad (13)$$

C being the concentration of the acid. Equating this in turn to E_{Br} and E_I, we obtain for the bromide $C = 0{\cdot}013\sqrt{C_H}$ (14), and for the iodide $C = 0{\cdot}12\sqrt{C_H}$ (15).

Two points must be mentioned with regard to the iodide cells, *viz.*, first, that the acidity must be kept very low—below $N/100$—because at higher concentrations the hydriodic acid reacts with the quinhydrone producing free iodine; and, secondly, that in the immediate neighbourhood of the end-point, equilibrium (and hence a reproducible potential) is only obtained after standing for ¼—½ hour with occasional shaking. Thus when high precision is required the titration of an iodide cannot be very expeditious.

7. "*Corrected Concentrations*": *Activities.*—For the sake of simplicity, the correction factors or activity coefficients, by which the concentrations are multiplied in the exact forms of the equations

given, have been ignored up to this point. It is, in fact, only when high precision is aimed at, and the most dilute solutions are titrated, that these factors need be considered; in such cases every symbol C, with or without subscript, representing a concentration (but not the symbols h, S_{AgCl}, S_{AgBr}, etc., which already represent activities), is to be multiplied by the appropriate activity coefficient, to make the formulæ exact.

EXPERIMENTAL.

8. *The Electrodes.*—The simpler the form of the electrodes the more easily is the surface layer of solution kept uniform with the rest by shaking.

The platinum electrodes are best free from glass so that they may the more easily be cleaned occasionally in hot sulphuric–chromic acid, and "blanked" by heating to redness for a minute or two in an alcohol flame. A form which has been found effective consists of a strip of thin foil, bent along its length to give a little rigidity, and fixed in a binding screw.

The silver halide electrodes have been made from pieces of stout silver wire about 15 cm. long by coating them, along a length of, say, 5 cm. from one end, with the appropriate halide. The wire is made the anode in the electrolysis of a dilute solution of the sodium or potassium salt, and a current of 2—3 milliamps. per sq. cm. is passed for about an hour. The wire should be turned once or twice to secure an even coating. Several electrodes can be prepared at one time, and they may be preserved in the dark for a week or more in corked tubes full of distilled water. In use, a silver halide electrode is fixed in a binding screw, and mounted in an ordinary clamp, vertically alongside and close to a platinum electrode, so that the pair will easily pass through the neck of a conical flask. We may speak of a "chloride-pair" of electrodes or a bromide- or iodide-pair, according to the nature of the silver halide electrode.

9. *The Reference Ion.*—We have seen that the potentials with which we have to deal in this method depend always on two ions, and the essential principle is that if we know the concentration of one of these ions roughly, we can titrate the other exactly. It will be convenient to speak of the ion of which the concentration must be roughly known as "the reference ion." Thus, in the titrations of the three halides the reference ion is the hydrogen ion, whilst in the titration of hydrogen ions (acids) it might be any of the three halides, but most commonly the chloride. Now in most cases, so long as the solution to be titrated is not weaker than about $N/100$ —the limit is lower in the case of bromide or iodide—*only the order of magnitude of the reference-ion concentration need be known* (see p. 2208). If, however, we are aiming at the highest precision in the

end-point, as in titrating extremely dilute solutions, we may need to know the reference-ion concentration to within a few units %, and a rough titration may be necessary to determine this.

If the reference ion is absent or nearly so, then we can easily introduce it in whatever concentration we require, by adding a little of a standard solution of sodium chloride (for Cl′) or of nitric or sulphuric acid (for H·).

It should be observed that, strictly speaking, it is the concentration at the end-point that has to be known or adjusted, and when the highest precision is required some allowance must be made for the dilution caused by the volume of reagent to be added; this can easily be done after a rough preliminary titration.

10. *The Method in its Simplest Form.*—The simplest form of procedure is applicable when the reference-ion concentration approximates to (see p. 2212), or can be adjusted roughly to, the values calculated from equations (9)—(12). All the physical apparatus required is a sturdy pointer-galvanometer (which will just detect, say, 10^{-7} amp.) in series with a rheostat, a tapping-key or plug, and one appropriate pair of electrodes, *viz.*, a chloride-pair for the titration of chloride or acid, a bromide- or an iodide-pair for the corresponding halide titrations. The deflexions of the galvanometer should be minimised by means of the rheostat so as to avoid any tendency to polarise the electrodes.

To the solution to be titrated, contained in a conical flask, a trace of quinhydrone is added (not more than 1 mg. per c.c. of solution), and most of it dissolved by gentle shaking. On raising the flask so that the pair of electrodes dips into the liquid, shaking gently, and then depressing the key, a marked deflexion of the galvanometer pointer is obtained with a high resistance in circuit, indicating a high *E.M.F.* (of the order of 0·2—0·3 volt). Some of the standard reagent is now added, and the observation of the *E.M.F.* then repeated, and so on, until eventually the *direction* of the pointer deflexion is reversed, the *E.M.F.* having reached and passed zero. This marks the end of the titration.

The indication is very sharp and sensitive. Thus the change from a deflexion representing an *E.M.F.* of 5 millivolts to the same deflexion in the reverse direction is produced, in 10 c.c. of solution, by the following quantities of reagent:

In titration of acid	3×10^{-8} g.-equiv.
„ „ „ chloride (or silver)	1×10^{-7} „
„ „ „ bromide (or silver)	6×10^{-9} „
„ „ „ iodide (slowly, see p. 2211) ...	$6{\cdot}5 \times 10^{-11}$ „

11. *The Use of the End-point Cell.*—When the concentration of the reference ion cannot conveniently be adjusted to the appropriate

value given above, it becomes necessary to add to the apparatus *either* a simple potentiometer *or* a second pair of electrodes—a chloride-pair—connected in opposition (platinum to platinum) to the first pair. In the latter case the end-point cell is completed by diluting some roughly standard hydrochloric acid approximately to the concentration C given in equation (5), (6), (14), or (15), dissolving a little quinhydrone in this solution contained in a flask or beaker, and raising the vessel on a support so that the second pair of electrodes dips into the solution. The vessel should be gently shaken occasionally during the titration.

Otherwise the titration proceeds exactly as described in Section 10, the end-point being indicated by the reversal of direction of the galvanometer deflexion, and the sensitivity being of the same order. The end-point cell can be used repeatedly for the same type of titration so long as the reference-ion concentration (C_{Cl} or C_H) in the titrated solutions remains the same.

12. *Alternative Use of a Potentiometer.*—If it is preferred to use a simple form of potentiometer to produce the end-point potential, instead of the end-point cell, it will be convenient, by means of equations (9), (10), (11), and (12), to construct tables after the following manner, giving the end-point potential for various values of the reference-ion concentration.

End-point Potential in Titration of Chloride (or Silver).

Acidity, C_H ...	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
End-pt. *E.M.F.*	0·1866	0·1292	0·0719	0·0145	−0·0428	−0·1002

For intermediate values:

To {multiply / divide} C_H by.....	1·25	1·6	2	2·5	3·2
Add to / Subtract from E the value ...	0·0055	0·0117	0·0173	0·0228	0·0290

These two tables, in conjunction with ordinary proportional interpolation, cover all probable values of C_H and E and similar tables are readily constructed for the other titrations. It would appear, however, that the second pair of electrodes, combined with a standard solution of hydrochloric acid and a measuring cylinder, constitutes a sort of "chemical potentiometer" which possesses advantages as regards bulk, cost, and immediate readiness for use over the simplest of physical instruments.

Results.

It would be superfluous to quote the results obtained in the more concentrated solutions, where the precision of the indication is greater than that of the volumetric apparatus. The results in

Table I, obtained with the more dilute solutions, indicate the limits of precision, and the order of accuracy attained requires no comment.

In order to provide a check on the *correctness* as well as the concordance of the results, the very dilute solutions were prepared by the precise dilution of carefully compared strong solutions. These gave the " calculated " results in the sixth column, from which the percentage deviations are given in the seventh column. $N/5$-Solutions of silver nitrate and the halides of potassium were compared by Volhard's method, and very good distilled water was used for the subsequent dilutions. The acid and alkali were compared at $N/2$-strength, and for the dilution of the baryta, conductivity water was used with a special arrangement to exclude atmospheric carbon dioxide.

TABLE I.

Solution titrated.	Reagent.	*R.I.A.*	*E.P.C.*	Vol. of reagent (c.c.). Found.	Calc.	Error, %.
100 C.c. of $\frac{N}{400}$-KCl	$\frac{N}{100}$-$AgNO_3$	1·0	0·0031	25·13	25·12	+0·04
		0·09	0·00093	25·135		+0·06
		0·00056	None	25·12		±0
200 C.c. of $\frac{N}{1000}$-KCl	$\frac{N}{100}$-$AgNO_3$	0·09	0·00093	20·11	20·095	+0·07
		0·01	0·00031	20·07		−0·12
		0·00056	None	20·08		−0·07
1000 C.c. of $\frac{N}{10000}$-KCl	$\frac{N}{100}$-$AgNO_3$	0·25	0·00155	10·08	10·05	+0·3
		0·04	0·00062	9·94		−1·1
		0·00056	None	9·97		−0·8
100 C.c. of $\frac{N}{5000}$-KBr	$\frac{N}{1000}$-$AgNO_3$	1·0	0·013	20·535	20·55	−0·07
		0·04	0·0026	20·53		−0·1
		$2·8 \times 10^{-5}$	None	20·56		+0·05
1000 C.c. of $\frac{N}{100000}$-KBr	$\frac{N}{1000}$-$AgNO_3$	0·09	0·0039	10·15	10·275	−1·25
		0·01	0·0013	10·22		−0·55
100 C.c. of $\frac{N}{5000}$-KI	$\frac{N}{1000}$-$AgNO_3$	0·01	0·012	20·04	20·01	+0·15
		0·0025	0·006	20·02		+0·05
1000 C.c. of $\frac{N}{100000}$-KI	$\frac{N}{1000}$-$AgNO_3$	0·0009	0·0036	9·95	10·005	−0·55
		$3·2 \times 10^{-7}$	None	10·10		+0·1
100 C.c. of $\frac{N}{400}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	1·0	0·0015	25·92	25·90	+0·08
		0·04	0·0003	25·89		−0·04
		0·0022	None	25·905		+0·02
200 C.c. of $\frac{N}{1000}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	0·25	0·00075	20·70	20·72	−0·1
		0·09	0·00045	20·71		−0·05
		0·0022	None	20·745		+0·12
1000 C.c. of $\frac{N}{10000}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	0·36	0·0009	10·50	10·36	+1·4
		0·09	0·00045	10·37		+0·1
		0·0022	None	10·45		+0·9

In the titrations a cheap pointer galvanometer was used throughout. The resistance of the titrated solutions was diminished by the addition of small quantities of a 10% potassium nitrate solution, prepared from Kahlbaum's " for analysis " product, twice recrystallised.

The activity coefficients depended largely on the added potassium nitrate. They were derived mainly by the use of Lewis and Randall's data (" Thermodynamics," McGraw Hill, New York, p. 382). In the third column are given the " corrected concentrations " or *activities* of the reference ion (*R.I.A.*) which were adjusted to some representative rounded values, while in the fourth column are given the activities of the hydrochloric acid in the end-point cells (*E.P.C.*), except where none was required.

Finally, it may be observed that the possibility of using a pair of very simple electrodes fixed close together and a single simple vessel for titration is not only a convenience, but also a simplification which permits the application of this method in several special ways (*e.g.*, microtitration), whilst the closeness of the electrodes and absence of liquid junction make it comparatively easy to keep the electrical resistance within bounds even at the lowest concentrations. Moreover, the elimination of the uncertainty attaching to liquid-junction potentials must facilitate greater precision.

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CCXCV.—*Nitrosation of Phenols. Part IV.* 3 : 5-*Dichlorophenol.*

By HERBERT HENRY HODGSON and JOHN SAMUEL WIGNALL.

THE object of this investigation was to extend the work of Hodgson and Moore (J., 1923, **123**, 2499) on the nitrosation of 3-chlorophenol to the case of 3 : 5-dichlorophenol.

Blanksma (*Rec. trav. chim.*, 1908, **27**, 25) claimed to have obtained 3 : 5-dichloro-4-nitrosophenol as a by-product in the conversion of 3 : 5-dichloroaniline to the phenol, and Willstätter and Schudel (*Ber.*, 1918, **51**, 782) stated that it was obtained by the addition of sulphuric acid to an aqueous solution of the sodium salt of 3 : 5-dichlorophenol and sodium nitrite. These products, however, gave

no Liebermann nitrosoamine reaction and proved to be identical with 3 : 5-*dichloro*-4-*nitrophenol*, prepared by direct nitration of 3 : 5-dichlorophenol. Willstätter and Schudel gave no analysis for chlorine, but recorded N, 6·95%, whereas the nitro- and nitroso-compounds require N, 6·7 and 7·3%, respectively.

After numerous unsuccessful attempts, both direct and indirect, to nitrosate 3 : 5-dichlorophenol, the required substance was obtained by the oxidation of 3 : 5-*dichloro*-4-*aminoanisole* with Caro's acid and subsequent hydrolysis of the 3 : 5-*dichloro*-4-*nitrosoanisole* by concentrated sulphuric acid.

3 : 5-Dichloro-4-nitrosoanisole is colourless, and, since 4-nitroso-anisole was described by Baeyer and Knorr (*Ber.*, 1902, **35**, 3035) as bluish-green, whilst 3-chloro-4-nitrosoanisole is now shown to be deep green, the suppression of colour may be ascribed to the chlorine atom in the 5-position.

A similar explanation would apply to the colourless 3 : 5-*dichloro*-4-*nitrosophenol*, which resembles the almost colourless 3-chloro-benzoquinone-4-oxime (Hodgson and Moore, *loc. cit.*), and may better be formulated as 3 : 5-dichlorobenzoquinone-4-oxime. Kehrmann's 2 : 6-dichlorobenzoquinone-4-oxime (*Ber.*, 1888, **21**, 3318) is light yellow and decomposes at 140°, whereas its colourless 3 : 5-isomeride decomposes at 165°.

Since 3-iodophenol on nitrosation behaves differently from 3-chloro- and 3-bromo-phenols (Hodgson and Moore, 1925, **127**, 2260), the direct nitrosation of 3-chloro-5-iodophenol was attempted, but without success.

During the attempts at nitrosation, it was found that nitrous acid nitrated 3 : 5-dichlorodimethylaniline in formic acid solution (the usual procedure was fruitless); the 3 : 5-dichloro-grouping has, therefore, the same effect as in 3 : 5-dichlorophenol, which is also nitrated by nitrous acid.

EXPERIMENTAL.

The initial material, 3 : 5-dichlorophenol, was prepared from trinitrobenzene (Hodgson and Wignall, J., 1926, 2077) and also by the following modification of Willstätter and Schudel's method (*loc. cit.*): 3 : 5-Dichloroaniline (26 g.) was dissolved in 220 c.c. of hot dilute sulphuric acid (2 : 9 by vol.), the mixture cooled, and diazotised at room temperature. Excess of nitrous acid was removed by carbamide (otherwise 3 : 5-dichloro-4-nitrophenol may be formed), and the mixture added gradually to a boiling solution of sulphuric acid (100 g.) in water (140 c.c.) through which steam was passing. The aqueous distillate was made alkaline, evaporated to very small bulk, cooled, and the 3 : 5-dichlorophenol (19·5 g.)

precipitated by careful addition of 30% sulphuric acid with vigorous stirring.

3 : 5-Dichlorophenol (16 g.) was nitrated in a solution of sodium nitrate (12 g.) in water (180 c.c.) at 90—100° by the gradual addition of 48 c.c. of dilute sulphuric acid (1 : 5) during 1 hour; the mixture was then heated on the water-bath for 2 hours and steam-distilled, 3 : 5-*dichloro*-2-*nitrophenol* (5 g.) passing over, and 3 : 5-*dichloro*-4-*nitrophenol* (6 g.) being obtained from the tarry residue by repeated extraction with hot dilute hydrochloric acid.

3 : 5-Dichloro-2-nitrophenol is moderately soluble in water and readily soluble in the usual organic solvents except light petroleum, from which it crystallises in lemon-yellow needles, m. p. 51° (Found : N, 6·5; Cl, 34·0. $C_6H_3O_3NCl_2$ requires N, 6·7; Cl, 34·1%); it does not form a hydrate (compare 3-chloro-2-nitrophenol, Hodgson and Moore, J., 1926, 155), and remains unchanged when kept for 2 hours at 110°. A solid acetate could not be obtained.

3 : 5-Dichloro-4-nitrophenol is readily soluble in the usual organic solvents except light petroleum, and crystallises from water in very pale yellow needles, m. p. 150° (Found : N, 6·7; Cl, 34·1%). The *acetate*, formed when a solution of the phenol in glacial acetic acid is warmed with acetyl chloride, crystallises from dilute alcohol in colourless needles, m. p. 99° (Found : Cl, 28·2. $C_8H_5O_4NCl_2$ requires Cl, 28·4%).

Action of Nitrous Acid on 3 : 5-*Dichlorophenol.*—This was carried out according to the directions both of Blanksma (*loc. cit.*) and of Willstätter and Schudel (*loc. cit.*). In each case a product of m. p. 150° [Found : N, (i) 6·8, (ii) 6·7; Cl, (i) 34·1, (ii) 34·2. Calc. for $C_6H_3O_3NCl_2$: N, 6·7; Cl, 34·3; calc. for $C_6H_3O_2NCl_2$: N, 7·3; Cl, 37·0%] was obtained, which was identical (mixed m. p. determination) with the 3 : 5-dichloro-4-nitrophenol above; the corresponding acetates were similarly shown to be identical.

Reduction of the 3 : 5-*Dichloro*-2- *and* -4-*nitrophenols.*—3 : 5-Dichloro-2- and -4-nitrophenols are reduced to the corresponding amino-phenols by dissolving them in 12 times their weight of water containing the theoretical amount of sodium carbonate and warming the solution on the water-bath with solid sodium hyposulphite until colourless. 3 : 5-*Dichloro*-2-*aminophenol* separates from the hot solution, but in the case of the 4-*amino*-isomeride the solution has to be cooled. 3 : 5-Dichloro-2-aminophenol is readily soluble in the usual organic solvents, except light petroleum, and crystallises from water in colourless needles, m. p. 132° (Found : Cl, 39·7. $C_6H_5ONCl_2$ requires Cl, 39·9%), which darken somewhat on keeping. Its aqueous solutions give a reddish-brown precipitate with ferric chloride. 3 : 5-Dichloro-4-aminophenol is less soluble in chloroform,

carbon tetrachloride, and carbon disulphide than its 2-amino-isomeride, but more soluble in water, from which it crystallises in colourless needles, m. p. 154° (Found : Cl, 39·8%). Its aqueous solutions give a violet coloration with ferric chloride.

3 : 5-*Dichloro*-2- and -4-*nitroanisoles* are prepared by boiling for 6 hours a mixture of the appropriate nitrophenol (6 g.) with xylene (60 c.c.) and potassium carbonate (12 g.) to which methyl sulphate (12 c.c.) is gradually added. After removal of the xylene, the anisoles can be obtained pure by steam-distillation. Yield, 70% in each case. 3 : 5-Dichloro-2-nitroanisole is much more volatile in steam than its 4-nitro-isomeride, and crystallises from methyl alcohol in colourless needles, m. p. 75° (Found : Cl, 31·7. $C_7H_5O_3NCl_2$ requires Cl, 32·0%). 3 : 5-Dichloro-4-nitroanisole crystallises from methyl alcohol in colourless needles, m. p. 70° (Found : Cl, 31·9%).

3 : 5-*Dichloro*-4-*aminoanisole* is prepared by reduction of the nitro-anisole (4·2 g.) with tin (3·5 g.) and concentrated hydrochloric acid (40 c.c.), and is finally removed by steam-distillation, being much more volatile than the parent nitro-anisole. It is very soluble in methyl alcohol and carbon tetrachloride, moderately soluble in light petroleum, and only slightly soluble in water or dilute acids; it crystallises from dilute methyl alcohol in colourless needles, m. p. 71° (Found : Cl, 36·7. $C_7H_7ONCl_2$ requires Cl, 37·0%).

3 : 5-*Dichloro*-4-*nitrosoanisole* was obtained by oxidation of the amino-anisole with Caro's acid as follows : Potassium persulphate (16 g.) was stirred into concentrated sulphuric acid (32 g.), kept at room temperature for 1 hour, then poured on ice and neutralised with potassium carbonate, the final volume being about 250 c.c. The mixture was rendered faintly acidic with acetic acid, added with stirring to a cold suspension of finely-divided 3 : 5-dichloro-4-amino-anisole (2·5 g.) in 200 c.c. of water, and kept for 24 hours, the stirring being maintained for the first 6 hours; the solid product was filtered off, and unchanged amine removed from it by extraction with warm very dilute hydrochloric acid. The crude product (1·5 g.; m. p. 122°) was crystallised from carbon tetrachloride and then from methyl alcohol; colourless needles, m. p. 125° (Found : Cl, 34·23. $C_7H_5O_2NCl_2$ requires Cl, 34·46%). The nitroso-anisole turns green on melting but becomes colourless again on solidifying, and is readily soluble in chloroform and acetone, but more sparingly soluble in carbon tetrachloride, benzene, and methyl alcohol, forming green solutions; it is insoluble in light petroleum and gives the Liebermann nitrosoamine reaction.

3 : 5-*Dichloro*-4-*nitrosophenol* [-*quinone*-4-*oxime*(?)] is obtained by heating 3 : 5-dichloro-4-nitrosoanisole (1 g.) with concentrated

sulphuric acid (10 c.c.) on the water-bath for ½ hour—longer periods produce charring. An odour of quinone is noticeable during the hydrolysis. On pouring the mixture on ice, a colourless solid separates, which completely dissolves in alkalis to a green solution. The product gives the Liebermann nitrosoamine reaction, is soluble in methyl alcohol, ether, acetone, and glacial acetic acid, sparingly soluble in water, benzene, nitrobenzene, and chloroform, and insoluble in light petroleum and carbon disulphide. It separates from dilute acetic acid in colourless leaflets, which turn light brown on exposure and decompose at 165° (Found: N, 7·4; Cl, 36·9. $C_6H_3O_2NCl_2$ requires N, 7·3; Cl, 37·0%). No change appears to be effected by alkalis but decomposition takes place with boiling acids.

Among the unsuccessful attempts to prepare the foregoing nitrosophenol may be mentioned the use of: (1) Aqueous solutions of the sodium salt of 3 : 5-dichlorophenol and sodium nitrite, which gave only the 4-nitrophenol on acidification under a variety of conditions; (2) formic and acetic acid solutions; (3) amyl nitrite (compare Henrich and Rodins, *Ber.*, 1902, **35**, 4192); (4) nitrosylsulphuric acid; (5) nitrous gases and an ethereal solution of 3 : 5-dichlorophenol. The materials used as the starting-point of indirect methods included (1) 3 : 5-dichlorodimethylaniline; (2) 3 : 5-dichloro-4-aminophenol (oxidation by Caro's acid; also diazotisation, followed by oxidation with ferricyanide).

An Example of Simultaneous Reduction and Chlorination.—Reduction of 3-chloro-4-nitroanisole (6 g.) with tin (6 g.) and concentrated hydrochloric acid (50 c.c.) gave 2·5 g. of 3 : 5-dichloro-4-aminoanisole. Iron and acetic acid, or tin and dilute hydrochloric acid, however, effected normal reduction to 3-chloro-4-aminoanisole (compare Hodgson and Handley, J., 1926, 542).

3-*Chloro*-4-*nitrosoanisole* is obtained when 3-chloro-4-aminoanisole hydrochloride (3·5 g.), dissolved in water (300 c.c.), is treated with sodium hydroxide (0·7 g.) then rendered faintly acidic with acetic acid, and oxidised by potassium persulphate (20 g.) as above. The product is almost insoluble in light petroleum, but readily dissolves in the usual organic solvents, forming green solutions; from methyl alcohol it crystallises in deep green needles, m. p. 59° (Found: Cl, 20·4. $C_7H_6O_2NCl$ requires Cl, 20·7%), which give the Liebermann nitrosoamine reaction.

Action of Nitrous Acid on 3 : 5-*Dichlorodimethylaniline.*—3 : 5-Dichlorodimethylaniline was best prepared by heating 3 : 5-dichloroaniline (8 g.), methyl sulphate (12 c.c.), and methyl alcohol (15 c.c.) for 5 hours in a sealed tube at 165—170° (great pressure is developed). The viscous red product was poured into water (100 c.c.) and kept

for 1 hour until solid. Yield 4 g. It crystallises from dilute methyl alcohol (charcoal) in colourless, rhombic plates, m. p. 55° (Found : Cl, 37·3. Calc. : Cl, 37·4%), which are readily soluble in the usual organic solvents.

Attempts to nitrosate this compound by the usual methods having proved fruitless, the following method was attempted : 3 : 5-Dichlorodimethylaniline (3·8 g.), dissolved in formic acid (15 c.c.), was treated at 0° with finely powdered sodium nitrite (1·4 g.). The brown needles which first formed rapidly became resinous, and, after separation, the product was extracted with a mixture of equal parts of alcohol and acetic acid and then recrystallised from methyl alcohol; golden needles, m. p. 142° (Found : Cl, 30·1. $C_6H_2NMe_2Cl_2 \cdot NO_2$ requires Cl, 30·2; $C_6H_2NMe_2Cl_2 \cdot NO$ requires Cl, 32·4%). This product is readily soluble in acetic acid but sparingly soluble in methyl alcohol.

Nitration of 3 : 5-*Dichlorodimethylaniline.*—To 3 g. of the dichlorodimethylaniline in concentrated sulphuric acid (12 c.c.) at 0°, nitric acid (1 c.c.; 91%) was gradually added during 1 hour. The mixture was kept for a further hour at 0°, then poured on ice, and the resulting solid was filtered off, washed with cold alcohol, and crystallised from methyl alcohol; golden needles, m. p. 142° (Found : Cl, 30·3%). This product, 3 : 5-*dichloro*-4-*nitrodimethylaniline*, was identical with the preceding substance (mixed m. p. determination), thereby establishing the fact that 3 : 5-dichlorodimethylaniline is nitrated by nitrous acid in formic acid solution.

3 : 5-Dichloro-4-nitro-dimethylaniline is not decomposed on boiling with aqueous alkaline hydroxides.

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 5th,* 1927.]

CCXCVI.—*The Abnormal Reaction of Certain Aromatic Aldehydes with Schiff's Reagent.*

By JOHN BALDWIN SHOESMITH, CHARLES EDWIN SOSSON, and ARTHUR CLEMENT HETHERINGTON.

WIELAND and SCHEUING (*Ber.*, 1921, **54**, 2527) have recently carried out an investigation on the nature of Schiff's reagent and the colour obtained in its reaction with aldehydes, and conclude that

the essental constituent of the reagent is an *N*-sulphinic acid of pararosaniline-*C*-leucosulphonic acid,

$$SO_3H\cdot C(C_6H_4\cdot NH_2)_2\cdot C_6H_4\cdot NH\cdot SO_2H.$$

To the soluble violet dyestuff produced on the admixture of the reagent with acetaldehyde they ascribe the formula

$$NH{:}C_6H_4{:}C[C_6H_4\cdot NH\cdot SO\cdot O\cdot CH(OH)\cdot CH_3]_2.$$

There are several references to abnormalities in the Schiff aldehyde reaction in the literature (compare Lorenz, *Ber.*, 1881, **14**, 789; Schmidt, *ibid.*, p. 1840; Bela von Bitto, *Z. anal. Chem.*, 1897, **36**, 369; Paula and von Buttlar, *Annalen*, 1911, **383**, 230), and one of us has remarked on the behaviour of salicylaldehyde (J., 1923, **123**, 2700) and β-resorcylaldehyde (*ibid.*, p. 2705) in giving yellow colorations and precipitates, in place of the usual soluble dyestuff, under certain conditions.

Investigations have been carried out with a view to discovering (1) the class of aldehyde which gives these abnormal yellow precipitates with Schiff's reagent; (2) the conditions under which these precipitates are formed—because it was afterwards discovered that red colorations and precipitates are produced under other conditions; and (3) the nature of this abnormal reaction and the composition of the precipitates.

Of the large number of aldehydes examined ortho-hydroxy-aromatic aldehydes most readily give yellow precipitates; indole-aldehyde behaves similarly. The reaction product is chiefly dependent on the quantity of sulphur dioxide capable of neutralising iodine (afterwards referred to as "free" sulphur dioxide) present in the reagent, as is seen from the Table, in which Y = yellow, O = orange, R = red, P = purple, B = brown, subscript p = precipitate, subscript c = coloration, and g. = g. of "free" sulphur dioxide per 100 c.c. of reagent.

	g. = 19	10	1·0	0·25	0·1
Aldehyde.			Reaction.		
Salicylaldehyde	P_c	P_p	Y_p	Y_p	Y_p
p-Hydroxybenzaldehyde	P_c	P_c	P_p	Y_p	Y_c
β-Resorcylaldehyde	P_p	Y_p	Y_p	Y_p	Y_p
Dihydroxy*iso*phthalaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2 : 3 : 4-Trihydroxybenzaldehyde	Y_c	Y_c	Y_c	Y_c	Y_c
p-Methoxysalicylaldehyde	R_p	R_c+Y_p	Y_p	Y_p	Y_p
Vanillin	P_p	B_p	Y_p	Y_p	Y_p
Orcylaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
α-Orcindialdehyde	R_p	Y_p	Y_p	Y_p	Y_p
Indole-3-aldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-3-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-4-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-5-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-1-naphthaldehyde	O_p	O_p	O_p	O_p	O_p
1-Hydroxy-2-naphthaldehyde	R_c+O_p	O_p	O_p	O_p	O_p
Cinnamaldehyde	P_p	P_p	P_p	B_p	B_p

The following aldehydes, chosen as representatives of other classes, behave normally, in that red or purple solutions are obtained under all the above conditions: Benzaldehyde, *m*-hydroxy-, and *o*-, *m*-, and *p*-methoxy-benzaldehydes; *o*-, *m*-, and *p*-nitro-, *o*-chloro-, *o*- and *m*-fluoro-, *m*- and *p*-bromo-, *p*-methyl-, 2-nitro-4-methoxy-,* 3-nitro-4-methoxy-benzaldehydes; 3 : 4-methylenedioxybenzaldehyde ($P_p + V_c$); *iso*propyl- and 2-carboxy-3 : 4-methylenedioxybenzaldehydes; α-naphthaldehyde, and its 3-* and 5-methoxy- and 5-bromo-derivatives; 5-bromo-2-naphthaldehyde; acrolein (deep blue), *iso*butyric aldehyde, glycollaldehyde, and glyoxal. It is noteworthy that 2 : 4-dimethoxybenzaldehyde, 2-methoxy-1-naphthaldehyde,† and thioacetaldehyde were neutral towards the reagent, and that resacetophenone and 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone gave a violet coloration very slowly—in sharp contrast to β-resorcylaldehyde, which reacts rapidly.

In general, *o*-hydroxy-aromatic aldehydes give the yellow precipitates most readily, but exceptions to the rule are afforded by *p*-hydroxybenzaldehyde, which gives the yellow reaction when only a trace of "free" sulphur dioxide is present, by vanillin, by cinnamaldehyde and indole-aldehyde.

In order to ascertain the composition of the precipitates, that obtained from β-resorcylaldehyde was examined in detail. They cannot be separated as pure compounds owing to their insolubility in organic solvents or water, and to their instability towards acids and alkali. Analytical results were therefore only approximate, but a satisfactory clue to the constitution of the precipitate in each case was obtained from the interaction of the aldehyde with reagents in which the base employed was analogous to pararosaniline.

Neither the yellow nor the red *precipitates* have a constitution approximating to that proposed by Wieland and Scheuing for the dyestuff. The two classes of precipitates have very nearly, but not quite, the same constitution. When they are first formed their behaviour corresponds with that which would be expected of sulphites of hydrated Schiff's bases formed from the aldehyde and pararosaniline-*C*-leucosulphonic acid, $SO_3H{\cdot}C(C_6H_4{\cdot}NH_2)_3$—the basic constituent of Schiff's reagent. These sulphites, on drying over calcium chloride or potassium hydroxide, slowly lose sulphur dioxide; and after complete removal of the "sulphite" sulphur dioxide by dilute aqueous sodium bicarbonate, the final dried

* These aldehydes have not been described in the literature and were prepared in connexion with other investigations, an account of which, it is hoped, will be published shortly.

† This is probably due to steric hindrance, because in another investigation it was found impossible to convert the aldehyde to the alcohol by the well-known methods which readily served in other cases.

substance has properties that would be associated with, and a composition approximating to that of, a hydrated Schiff's base of formula $SO_3H\cdot C[C_6H_4\cdot NH\cdot CH(OH)\cdot C_6H_3(OH)_2]_3$. On careful hydrolysis with 10% aqueous sodium hydroxide, in which the precipitates are soluble, it was possible to recover the aldehyde in a quantity corresponding to that expected from the above formula, but the recovered pararosaniline could not be estimated. Hence we regard the reaction with this type of aldehyde as being $SO_3H\cdot C(C_6H_4\cdot NH_2)_3 + 3R\cdot CHO + xH_2SO_3 \longrightarrow SO_3H\cdot C[C_6H_4\cdot NH\cdot CH(OH)R]_3(H_2SO_3)_x$, the sulphurous acid acting as a catalyst in the formation of the "Schiff's base."

This suggestion is substantiated by the production of the yellow precipitates from pure pararosaniline-*C*-leucosulphonic acid and β-resorcylaldehyde in sulphurous acid solution, and also of precipitates, which are analogous in appearance, constitution, and general properties, from the aldehyde and the following: (*a*) the leucosulphonic acid in hydrochloric acid solution, this acid taking the place of sulphurous acid as a catalyst, and the resulting precipitate being a hydrochloride, and not a sulphite; (*b*) sulphurous acid solutions of *p'p''p'''*-triaminotriphenylmethane; (*c*) *p'p''*-diaminotriphenylcarbinol; (*d*) *p'p''*-diaminotriphenylmethane; or (*e*) *p*-aminotriphenylmethane. It was not possible to obtain the simplest analogue of Schiff's reagent, *i.e.*, a sulphurous acid solution of *p*-aminotriphenylcarbinol.

The reaction of Schiff's reagent in the normal case is considered by Wieland and Scheuing to involve the production of a compound in which carbon and nitrogen are indirectly united through sulphur dioxide, *i.e.*, the formation of an aldehyde-bisulphite type, whilst in the abnormal cases the C–N union is direct, *i.e.*, of the Schiff's base or anil type. The presence of large quantities of sulphur dioxide in the reagent favours the bisulphite reaction and also retards the Schiff's base reaction, and thus in some of the cases examined, *e.g.*, salicylaldehyde, a small quantity of the red dyestuff is produced with Schiff's reagent saturated with sulphur dioxide. The red precipitates are therefore really yellow ones which have adsorbed a little of the red dyestuff, but not sufficient to make the analytical results for the two classes markedly different.

It is not yet understood why the aldehydes given above should behave in this abnormal manner towards Schiff's reagent.

EXPERIMENTAL.

Reaction of β-Resorcylaldehyde towards Schiff's Reagent.

The reagent was prepared by allowing 10 g. of pure pararosaniline (Kahlbaum) to stand at the ordinary temperature in 500 c.c. of

saturated aqueous sulphur dioxide; when the solution became colourless 200 c.c. were added to a (saturated) solution of 8 g. of β-resorcylaldehyde in 1000 c.c. of water at 20°. The freshly prepared reagent produced a red coloration followed by a red precipitate; a yellow precipitate then formed slowly under ordinary conditions, but very rapidly if sulphur dioxide was removed from the solution under diminished pressure. From a separate portion of the reagent, the sulphur dioxide was removed, and samples were used at various concentrations of "free" sulphur dioxide (1) to estimate the amount of sulphur dioxide present, by titration with iodine, and (2) to investigate the effect of loss of sulphur dioxide from the reagent on the nature of the reaction. The results are summarised on p. 2222.

The solids were filtered and they then dissolved in aqueous alkali—the yellow with an orange colour, the red with a purple colour—and from these solutions the original solid could be immediately reprecipitated by the addition of acid. If allowed to stand in such a solution, the solids were hydrolysed (very rapidly if the solutions were heated) and a purple solid, pararosaniline, was precipitated along with a little tar. After this was filtered off, acidification of the alkaline solution produced a strong odour of sulphur dioxide, and β-resorcylaldehyde could be extracted from the acid liquid with ether, thus showing the essential constitution of the solids to be: aldehyde, pararosaniline, and sulphur dioxide.

For analysis, the solids were filtered and dried in a desiccator. The red remained unchanged in colour, but the yellow slowly lost sulphur dioxide and water, becoming dark green, and only became yellow again on the addition of *sulphurous acid*, and not on the addition of either water or sulphur dioxide alone. The loss of sulphur dioxide and the concomitant colour change were continuous as shown by sulphur estimations (see below) at intervals. The last trace of sulphur remaining in the solids as sulphite (but not that on the central carbon atoms of the rosaniline) was removed by dilute aqueous sodium bicarbonate, which caused the sample which was originally yellow to become deep green, but did not affect the colour of the red sample.

Sulphur estimations (*Carius*). Yellow solid: 2 days, 7·16; 1 week, 5·6; 2 months, 4·0; after washing with $NaHCO_3$, 2·8%. (Last sample had N, 4·4%.) Red solid: 1 week, 6·0; 2 months, 4·3; after washing with $NaHCO_3$, 3·2%. (Last sample had N, 5·1%.) The last sample from the yellow compound, which had been thoroughly dried over calcium chloride, was further dried over concentrated sulphuric acid in a vacuum. The last treatment caused a loss of 7·2%, which is ascribed to loss of water from any

–NH·CH(OH)– groups present (compare Dimroth and Zoeppritz, *Ber.*, 1902, **35**, 996).

In order to demonstrate the catalytic action of the sulphurous acid, pararosaniline-*C*-leucosulphonic acid (Wieland and Scheuing, *loc. cit.*) was dissolved in (*a*) sulphurous acid and (*b*) dilute hydrochloric acid, and on the addition of an aqueous solution of β-resorcylaldehyde to these solutions, a yellow precipitate {Found: N, 4·4; S, 2·9. $SO_3H·C[C_6H_4·NH·CH(OH)·C_6H_3(OH)_2]_3$ requires N, 5·4; S, 4·1%} was produced in the former case, identical in all respects with that from the aldehyde and Schiff's reagent, and a greenish-yellow precipitate {Found: N, 4·4; Cl, 8·5; S, 2·75. $SO_3H·C[C_6H_4·NH·CH(OH)·C_6H_3(OH)_2,HCl]_3$ requires N, 4·7; Cl, 11·8; S, 3·5%} in the latter case; this differed from the yellow precipitate in containing hydrolysable chlorine, *i.e.*, it was the hydrochloride instead of the sulphite. Since it was impossible to recrystallise either of the solids, the analytical results only approximate to those of pure compounds, and it appears as if some of the nitrogen atoms combined with two aldehyde residues, causing the low results for S, N, and Cl.

The quantity of aldehyde present in the precipitate was determined as follows, the method being trustworthy to within ± 2%: A weighed quantity of the solid was hydrolysed with boiling 8% aqueous sodium hydroxide, the solution cooled, filtered from pararosaniline, almost neutralised with dilute hydrochloric acid, and made up to 50 c.c. Phenolphthalein was added, followed by hydrochloric acid drop by drop until the solution was just colourless; methyl-orange was then added and the solution titrated with standard acid. This was a measure of the aldehyde in the original compound, since β-resorcylaldehyde is acid to phenolphthalein,* but does not affect methyl-orange. An addition of 0·1 c.c. of the acid was required to correct for the change from p_H 7—9 (sensitivity to phenolphthalein) to p_H 3—5 (sensitivity to methyl-orange). The yellow solid contained 56% of aldehyde, and the red 50%; $SO_3H·C[C_6H_4·NH·CH(OH)·C_6H_3(OH)_2]_3$ requires 52%. The aldehyde content should be higher than that given by the titration method but the tar probably contained a little aldehyde which resisted aqueous extraction.

Influence of Sulphurous and Hydrochloric Acids on the Rate of Precipitation of Schiff's Base.—A standard solution of each acid

* Although β-resorcylaldehyde behaves as a monobasic acid towards alkali in presence of phenolphthalein (compare *Annalen*, 1911, **383**, 288), 4 : 6-dihydroxy*iso*phthalaldehyde behaves partly as a mono- and partly as a di-basic acid, and cannot be estimated in the same manner.

was in turn added to a dilute aqueous solution of aniline (3%), which was then immediately added to a 5% solution of β-resorcylaldehyde, the tube shaken, and the time (t) noted for the appearance of the precipitate. In each case, increasing concentration of acid first diminished and then increased the time required :

G. of SO_2 per 100 c.c. of solution.	t (secs.).	G. of HCl per 100 c.c. of solution.	t (secs.).
0·0	115	0·0	110
0·026	75	0·0073	100
0·066	60	0·0803	15
0·092	20	0·3285	15
0·118	20	0·4280	20
0·170	45	0·5840	95
0·298	200	0·8760	>300

*Condensation of Resorcylaldehyde with Bases analogous to Triphenylmethane-*C*-leucosulphonic Acid.*

Preparation of Bases.—p′p″p‴-*Triaminotriphenylmethane.* Finely powdered, dried triphenylmethane (10 g.) was slowly added to a constantly stirred mixture of 78 g. of nitric acid (d 1·42) and 120 g. of concentrated sulphuric acid at — 5—0°, and after the temperature of the whole had been allowed to rise slowly to about 15° (½ hour), the reaction mixture was poured into much cold water, and the solid trinitrotriphenylmethane was filtered off, boiled with 75% acetic acid, filtered, dried, and recrystallised from chloroform–ether; m. p. 212·5° (yield, 65%).

The trinitro-compound was dissolved in boiling glacial acetic acid, and to the red solution zinc powder was added until the colour had disappeared. The whole was diluted with water, excess of zinc filtered off, ammonia added to the solution, and the base filtered, dried, dissolved in dilute hydrochloric acid, the hydrochloride precipitated by the addition of concentrated hydrochloric acid, and finally dissolved in water, from which the free base was precipitated with ammonia, filtered, dried, and recrystallised from absolute alcohol. It had m. p. 201°.

pp′-*Diaminotriphenylmethane.* This was prepared by a slight modification of Baeyer and Villiger's method (*Ber.*, 1904, **37**, 2860); part of it was acetylated, and the diacetyl derivative (m. p. 233—234°) was oxidised to the carbinol, which was purified by conversion to the hydrochloride (Doebner's violet) and reprecipitation with ammonia. It had m. p. 173°.

p-*Aminotriphenylmethane.* A mixture of benzhydrol (5 g.) (from benzophenone), aniline hydrochloride (3·5 g.), and powdered anhydrous zinc chloride (4 g.) was immersed for 20 hours in the vapour of a mixture of toluene and xylene at 140°—this temperature

is of extreme importance. The whole was cooled, the tube broken, washed with water, shaken with a mixture of ether and sulphuric acid, and the curdy, insoluble amine sulphate filtered off, recrystallised from water, dried, extracted with ether (Soxhlet) until no brown coloration of the ether was observed, and finally dissolved in much boiling water; the base was then precipitated by sodium hydroxide and crystallised from light petroleum (aggregates of colourless plates, m. p. 84·5°). The acetyl derivative had m. p. 167° (compare Baeyer and Villiger, *loc. cit.*).

p-*Aminotriphenylcarbinol.* The methane was oxidised as in the case of the diamino-compound (compare Baeyer and Lohr, *Ber.*, 1890, **23**, 1623). *p*-Acetamidotriphenylcarbinol crystallises in fine, lustrous needles, m. p. 175·5°. To obtain the free amine, the pure acetyl derivative (4·5 g.) was mixed with 250 c.c. of dilute sulphuric acid (1 in 5) and 30 c.c. of alcohol, and the whole was boiled until clear (3 hours). The solution was filtered and caustic soda added to the hot filtrate (not sufficient to neutralise it) until a few drops gave a crystalline deposit on cooling. The bulk of the solution was then allowed to cool, and the aminotriphenylcarbinol sulphate crystallised in orange plates, which were dried and extracted in a Soxhlet, as in the case of the diamino-compound. The pure sulphate was then dissolved in hot water and the base precipitated with ammonia. It had m. p. 115°, but could not be obtained in a crystalline condition from any solvent (compare Baeyer and Lohr, *loc. cit.*).

Unlike the di- and tri-amino-derivatives, the mono-amino-carbinol is not readily soluble in sulphurous acid, and in an attempt to prepare the *C*-leucosulphonic acid by dissolving the carbinol in hot sulphurous acid solution, a crystalline solid was obtained of m. p. 125—128° (decomp.) (Found: N, 3·72; S, 5·6). The compound most nearly corresponding to this is the sulphite

$$[(C_6H_5)_2C(OH)\cdot C_6H_4\cdot NH_2]_2,H_2SO_3,$$

which requires N, 4·4; S, 5·1%. When heated on the water-bath, the crystals became deep orange in colour, in agreement with the fact that feebly coloured salts of the carbinol become deeply coloured when heated. Hence the *C*-leucosulphonic acid could not be obtained because of the insoluble nature of the sulphite first formed on the addition of sulphurous acid to the carbinol.

Aqueous solutions of the aldehyde were mixed with sulphurous acid solutions of the above bases in order to trace the regularity in sulphur and nitrogen content of the precipitates. The estimations were carried out after the solids had been washed with aqueous sodium bicarbonate and dried, and the results are summarised as follows.

Amine.	N%.	S%.	Calc. for 1 aldehyde to each NH_2-group N%.	S%.
$CH(C_6H_4\cdot NH_2)_3$	5·3	trace	5·97	0·0
$CHPh(C_6H_4\cdot NH_2)_2$	4·6	,,	5·06	0·0
$CPh(OH)(C_6H_4\cdot NH_2)_2$	4·1	3·4	4·43	5·1
$CHPh_2\cdot C_6H_4\cdot NH_2$	3·5	0·0	3·5	0·0

It is thus seen that only in the cases of the carbinols where *C*-leucosulphonic acids are formed is any appreciable quantity of sulphur left in the solids, and the proportion of nitrogen falls quite regularly with number of amino-groups present. It is also noteworthy that all the precipitates contained sulphur until washed with dilute bicarbonate, and that the colour change was not so marked in the case of the methanes as the carbinols.

Condensations of Other Aldehydes with Schiff's Reagent.—The aldehydes used here were prepared by the methods given in the literature.* The majority of these were almost insoluble in water and hence were first dissolved in alcohol, which had to be freed from traces of aldehyde. For this purpose it was boiled with solid caustic soda and distilled, the middle fraction being mixed with about 2 c.c. of Schiff's reagent and again fractionated; the first portion was rejected, but about 1 l. of alcohol, which gave a very faint pink colour with Schiff's reagent only after the lapse of ½ hour, was thus obtained. The aldehyde to be tested (0·25 g. approx.) was then dissolved in 5 c.c. of the alcohol, 5 c.c. of the reagent (made up as before) were added, and the mixture was very gently shaken to avoid atmospheric oxidation of the alcohol. The results are given on p. 2222.

Note on the Stability of Schiff's Reagent.—As is well known, Schiff's reagent when heated develops a red colour similar to that obtained in normal aldehyde reactions. It has been found that this colour disappears when the solution is cooled if it has not been either boiled or heated for a considerable time, for the appearance and disappearance of the colour depend on the amount of sulphur dioxide present in this solution. Damianovich (*Chem. Abs.*, 1910, **4**, 1681) heated Schiff's reagent in a sealed tube, and therefore noted the same phenomenon. *pp'*-Diaminotriphenylcarbinol behaves in exactly the same way, the development of a deep violet colour in the heat and its disappearance in the cold being very striking. Absorption spectra were photographed and the bands were almost identical in the first case with those observed in pararosaniline hydrochloride, and in the second case with those in Doebner's violet. A colour change was also noted in the case of

* Neither orcinol nor indole condenses with diphenylformamidine to give an aldehyde-anil (compare Shoesmith and Haldane, J., 1923, **123**, 2705).

the mono-amino-compound and here the hot solution was yellow and the cold colourless, but for reasons given this was not so satisfactory as the others. Wieland and Scheuing (*loc. cit.*) have proved that when Schiff's reagent is boiled until a precipitate appears the following reaction takes place:

$$2C(NH_2\cdot C_6H_4)_2(SO_3H)\cdot C_6H_4\cdot NH\cdot SO_2H \longrightarrow \underset{(A.)}{} \quad \underset{(B.)}{C(NH_2\cdot C_6H_4)_3\cdot SO_3\cdot NH_2{:}C_6H_4{:}C(C_6H_4\cdot NH_2)_2}.$$

The formation of the colour suggests that an intermediate stage has been observed and that the full cycle of changes is as follows:

$$A \underset{\text{Cooled (SO}_2\text{ regained by C)}}{\overset{\text{Heated (SO}_2\text{ lost to solution)}}{\rightleftharpoons}} \underset{(C.)}{(NH_2\cdot C_6H_4)_3C\cdot SO_3H} \overset{\text{Further heating}}{\underset{\text{Cooling}}{\rightleftharpoons}} \underset{(D;\ \text{coloured})}{(NH_2\cdot C_6H_4)_2C{:}C_6H_4{:}NH,H_2SO_3}$$

$$\Big\downarrow \text{Loss of } SO_2 \text{ from boiling solution}$$

$$(NH_2\cdot C_6H_4)_2C{:}C_6H_4{:}NH \quad (E.)$$

Unchanged C combines with E to form B by salt formation.

In order to avoid this disadvantage of Schiff's reagent, a "modified reagent" has been suggested independently by Prudhomme (*Bull. Soc. Ind. Mulhouse*, 1904, **74**, 169) and by Wertheim (*J. Amer. Chem. Soc.*, 1922, **44**, 1834), which is prepared from pararosaniline and sodium hyposulphite. Towards such a reagent the *o*-hydroxybenzaldehydes behave as towards a Schiff's reagent containing about 1 g. of "free" sulphur dioxide per 100 c.c.

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CCXCVII.—*The Action of Phosphorus Pentabromide on the Isomeric β-Methoxyphenylethyl Alcohols.*

By JOHN BALDWIN SHOESMITH and ROBERT JORDAN CONNOR.

DURING attempts to prepare the isomeric β-methoxyphenylethyl bromides by the method which served for the corresponding methyl derivatives (Shoesmith and Connor, this vol., p. 1768), it has been discovered that when the phosphorus pentabromide reacts with the isomeric β-methoxyphenylethyl alcohols, the nuclear directing power of the methoxyl group is so great that it causes the formation of

nuclear-brominated derivatives of the expected β-methoxyphenylethyl bromides. Thus the only compounds isolated in a pure state are β-5-*bromo*-2-*methoxyphenylethyl bromide* from the ortho-alcohol, β-6-*bromo*-3-*methoxyphenylethyl bromide* from the meta-, and β-3-*bromo*-4-*methoxyphenylethyl bromide* from the para-alcohol. The orientation of the disubstituted β-phenylethyl bromides has been proved in each case by oxidation to the corresponding known bromomethoxybenzoic acid.

Whilst carrying out preliminary experiments on the most satisfactory methods for obtaining substituted β-phenylethyl alcohols, the authors found that β-phenylethylamine in aqueous hydrochloric acid yields with nitrous acid an appreciable quantity of β-phenylethyl chloride in sharp contrast to the production of pure alcohols from the isomeric tolylmethylamines (Shoesmith and Slater, J., 1924, **125**, 2278).

Experimental.

Three series of reactions by which the isomeric β-methoxyphenylethyl alcohols might conceivably be prepared were investigated:

(1) $R\cdot CHO \xrightarrow{CH_2(CO_2H)_2} CHR{:}CH\cdot CO_2H \xrightarrow[\text{amalg.}]{Na} CH_2R\cdot CH_2\cdot CO_2H \xrightarrow[+NH_3]{SOCl_2} CH_2R\cdot CH_2\cdot CONH_2 \xrightarrow{NaOCl} CH_2R\cdot CH_2\cdot NH_2 \xrightarrow{HNO_2} CH_2R\cdot CH_2\cdot OH$ (Haworth, Perkin, and Rankin, J., 1924, **125**, 169).

(2) $R\cdot CHO \xrightarrow[+\text{alkali}]{CH_3NO_2} CHR{:}CH\cdot NO_2 \xrightarrow[\text{acid}]{Zn+} CH_2R\cdot CH{:}NOH \xrightarrow[\text{amalg.}]{Na} CH_2R\cdot CH_2\cdot NH_2 \longrightarrow CH_2R\cdot CH_2\cdot OH$ (Rosenmund, *Ber.*, 1909, **42**, 4778).

(3) $R\cdot Br \xrightarrow[CH_2Cl\cdot CH_2OH]{Mg+} CH_2R\cdot CH_2\cdot OH$ (Grignard, *Compt. rend.*, 1905, **141**, 44).

The yield of amine obtained by scheme (1) was much better than that by (2), but the poor yield of alcohol from amine led to the adoption of (3), which involved the laborious preparation of large quantities of the isomeric bromoanisoles.

The following is the best method for the preparation of *o*-methoxybenzaldehyde [used in (1) and (2)] in quantity: Salicylaldehyde (122 g.) was emulsified in a flask fitted with a reflux condenser by vigorous stirring with 40 c.c. of water, and a solution of potassium hydroxide (85 g. in 160 c.c. of water) added alternately with methyl sulphate (157 g.). The appearance and disappearance of the yellow colour of the potassium compound of the aldehyde served as an excellent indication of the course of the reaction; excess of alkali was avoided and hence the reaction temperature could be allowed to

rise without affecting the yield, which was always about 100 g., b. p. 236—237°.

The amines obtained in series (1) had b.p.'s as follows: R = C_6H_5, 88—89°/18 mm.; R = *o*-MeO·C_6H_4, 127—128°/21 mm.; R = *m*-MeO·C_6H_4, 126—127°/14 mm.; R = *p*-MeO·C_6H_4, 131—132°/18 mm.

Action of Nitrous Acid on β-Phenylethylamine in Hydrochloric Acid Solution.—The amine hydrochloride, precipitated from a benzene solution of the amine by hydrogen chloride, was dissolved in a small quantity of water, and dilute hydrochloric acid added, followed by an aqueous solution of sodium nitrite. The whole was allowed to stand for 2 hours and the reaction was completed by 30 minutes' heating on the water-bath. The oil was extracted with ether, washed, dried, and distilled, the lowest fraction, b. p. 82—87°/21 mm., being collected separately. It was a colourless, non-pungent oil, containing hydrolysable chlorine, and when treated with fuming nitric acid at —15° (compare Barger, J., 1909, **95**, 2193) it yielded β-*p*-nitrophenylethyl chloride, m. p. 46—47°, unaltered by admixture with an authentic specimen. When sulphuric acid was employed in place of hydrochloric acid only very small, impure yields were obtained.

As examples of the methods used in scheme (2), the following are given, since the compounds have not been previously described.

m-*Methoxy-ω-nitrostyrene.*—To a vigorously stirred solution of *m*-methoxybenzaldehyde (28 g.) and nitromethane (13 g.) in alcohol (40 c.c.), 25% methyl-alcoholic potassium hydroxide (23 c.c.) was slowly added, followed by a solution of sodium hydroxide (4 g. in 20 c.c. of water), after which the almost solid product was poured into ice-water and, when *completely in solution*, decomposed with the calculated quantity of ice-cold sulphuric acid; the crude yellow m-*methoxy-ω-nitrostyrene* was filtered, washed, and dried. It crystallised from alcohol in light yellow plates, m. p. 93—94° (Found: N, 8·0. $C_9H_9NO_3$ requires N, 7·8%).

The nitrostyrene (13 g.) was mixed with zinc dust (13 g.) and the mixture added to a vigorously stirred solution of 25 c.c. of glacial acetic acid in 65 c.c. of alcohol, the temperature being kept at 35°. After 10 minutes, alcohol (20 c.c.) was added, and when the temperature had fallen to 15° the solid was filtered off and extracted with ether; the extract was washed with aqueous sodium carbonate and then extracted with sodium hydroxide. m-*Methoxyphenylacetaldoxime* was precipitated from this on the addition of sodium bicarbonate, and was filtered, washed, dried, and recrystallised from ligroin, and finally from water; white needles, m. p. 92·5—93° (Found: N, 8·5. $C_9H_{11}NO_2$ requires N, 8·5%).

From this oxime in alcoholic acetic acid only a very small quantity of β-*m*-methoxyphenylethylamine could be obtained by the action of 3% sodium amalgam.

Action of Phosphorus Pentabromide on β-o-*Methoxyphenylethyl Alcohol.*—o-Bromoanisole, b. p. 220°/744 mm., prepared by the action of methyl sulphate on *o*-bromophenol, was converted into β-o-*methoxyphenylethyl alcohol* in the manner already described (Shoesmith and Connor, *loc. cit.*). It is a colourless liquid, b. p. 130—131°/11 mm. (Found: C, 71·8; H, 7·77. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%). The alcohol (10 g.) was slowly added to phosphorus pentabromide (35 g.) in dry benzene (50 c.c.), the whole being cooled in ice-water. After 30 minutes, dry air was slowly drawn through the solution for 4 hours during which time the pentabromide slowly disappeared. The solution was then washed with ice-water, dried, the benzene distilled, and the residue fractionated under diminished pressure. No definite fraction could be separated other than one at 160—165°/12 mm., which solidified and crystallised from alcohol in fine, non-pungent, white needles of β-5-*bromo*-2-*methoxyphenylethyl bromide*, m. p. 55° [Found: C, 36·9; H, 3·5; Br (total), 53·7; Br (hydrolysable), 27·2. $C_9H_{10}OBr_2$ requires C, 36·7; H, 3·4; Br (total), 54·4; Br (hydrolysable), 27·2%].

The compound resisted oxidation with alkaline permanganate but was oxidised finally according to the scheme $CH_2R{\cdot}CH_2Br \xrightarrow[KOH]{alc.} CHR{:}CH_2 \xrightarrow[+H_2SO_4]{K_2Cr_2O_7} R{\cdot}CO_2H$. Approximately 0·5 g. of the bromide was heated on the water-bath for 30 minutes with 5 c.c. of 20% alcoholic potassium hydroxide; the whole was diluted with water, extracted with ether, the ether distilled, and the residue boiled for 3 hours with 1·2 g. of potassium dichromate and 7 c.c. of 20% sulphuric acid; the resinous oxidation product was separated and boiled with aqueous sodium hydroxide, excess of dilute hydrochloric acid was added, the liberated acid was extracted with ether, and the ether solution in turn extracted with sodium carbonate, from which on acidification and ether-extraction an acid was obtained. Recrystallised from water, it had m. p. 118—119°. 5-Bromo-2-methoxybenzoic acid has m. p. 119° (compare *Gazzetta*, 1886, **16**, 408). This established the constitution of the bromide as above.

Action of Phosphorus Pentabromide on β-m-*Methoxyphenylethyl Alcohol.*—*m*-Bromonitrobenzene was reduced to *m*-bromoaniline by West's method (J., 1925, **127**, 994) and converted into *m*-bromophenol (compare B.P. 200714)—for the necessary details of this process we are greatly indebted to Dr. H. H. Hodgson. This phenol with methyl sulphate gave *m*-bromoanisole, b. p. 214°/729 mm.,

which was then converted into β-m-*methoxyphenylethyl alcohol* in the usual manner. The alcohol is a colourless liquid, b. p. 135—137°/12 mm. (Found: C, 71·1; H, 7·6%).

When the alcohol was treated with phosphorus pentabromide, as in the previous case, no definite fraction could be separated, but when excess of pentabromide was used in the cold, a colourless, non-lachrymatory, non-pungent oil, b. p. 163—165°/13 mm., was isolated [Found: Br (total), 53·8; Br (hydrolysable), 27·2%]. The compound was oxidised much more readily than its isomeride, and gave an acid, m. p. 160—161°, which did not depress the m. p. of an authentic sample of 6-bromo-3-methoxybenzoic acid (J., 1925, **127**, 880), kindly supplied by Dr. H. H. Hodgson. This characterised the oil as β-6-*bromo*-3-*methoxyphenylethyl bromide*.

Action of Phosphorus Pentabromide on β-p-*Methoxyphenylethyl Alcohol.*—The alcohol was obtained from *p*-bromoanisole in the usual manner, and when purified had b. p. 138—140°/11 mm., m. p. 24° (compare Grignard, *loc. cit.*). When 1 mol. of pentabromide was used per mol. of alcohol, a colourless oil, b. p. 130—131°/11 mm., was obtained, which was almost pure β-p-*methoxyphenylethyl bromide* [Found: Br (hydrolysable), 35·0. $C_9H_{11}OBr$ requires Br (hydrolysable), 37·2%]. It was non-pungent and non-lachrymatory, and very similar in properties to the β-tolylethyl bromides (Shoesmith and Connor, *loc. cit.*), but further fractionation produced no improvement in the quality of the sample. With excess of pentabromide a colourless oil of b. p. 187—188°/19 mm. was formed [Found: Br (hydrolysable), 27·0%]. From this oil an acid of m. p. 217° was obtained on oxidation. 3-Bromo-4-methoxybenzoic acid has m. p. 218° (Balbiano, *Gazzetta*, 1881, **11**, 406), and the oil was therefore β-3-*bromo*-4-*methoxyphenylethyl bromide*.

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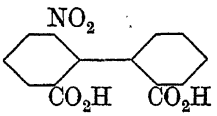
CCXCVIII.—*Investigations in the Diphenyl Series. Part VII. The Relative Stability of Optically Active Diphenic Acids.*

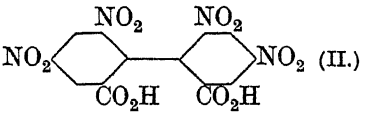
By FRANK BELL and PERCY HARRY ROBINSON.

THE theory advanced to account for the asymmetry of certain diphenyl derivatives (Part VI, this vol., p. 1695; *J. Soc. Chem. Ind.*, 1926, **45**, 864) definitely indicates that the optical activity

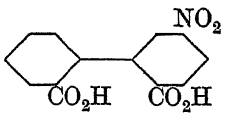
of such compounds should gain in permanence with an increase in the number of groups in the central positions. Up to the present, it has not proved possible to prepare in an optically active condition a compound with only two central groups, although some of the alkaloidal salts of "non-resolvable" acids show marked heterogeneity (compare Christie and Kenner, J., 1923, **123**, 779; 1926, 470).

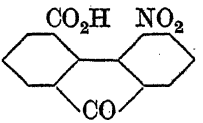
It is now found that 6-nitrodiphenic acid (I) is very much less optically stable than 4 : 4′ : 6 : 6′-tetranitrodiphenic acid (II). Thus

(I.) 

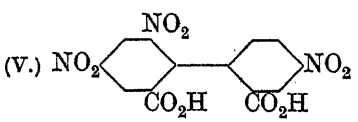
 (II.)

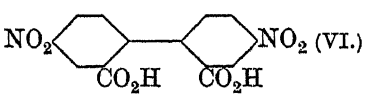
an aqueous solution of the sodium salt of the former acid steadily falls in rotatory power, whilst no such change can be perceived in the case of the latter acid. Further, boiling acetic anhydride racemises 6-nitrodiphenic acid in a very short time, whilst 4 : 4′ : 6 : 6′-tetranitrodiphenic acid loses only 25% of its activity after boiling with acetic anhydride for 10 hours. The failure which has attended attempts to resolve 5-nitrodiphenic acid (III) and 2 : 2′-dinitrodiphenyl-4 : 4′-dicarboxylic acid could have been anticipated from

(III.) 

 (IV.)

the "obstacle" theory. It may be noted that 5-nitrodiphenic acid readily forms an *anhydride*, and with sulphuric acid easily undergoes condensation to form a *fluorenone* derivative, in marked contrast to 4 : 4′ : 6′-trinitrodiphenic acid (V) which is unaffected

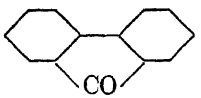
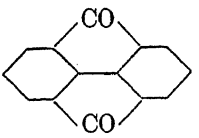
(V.) 

 (VI.)

by sulphuric acid at 160°. 4 : 4′-Dinitrodiphenic acid (VI) also does not undergo fluorenone formation (Underwood and Kochmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2069).

Although the failure to resolve fluorenone-4-carboxylic acid has been already reported by Mills, Palmer, and Tomkinson (J., 1924, **125**, 2365), it appeared possible that the introduction of a nitro-group in position 5 might stabilise the enantiomorphous forms which arise if the fluorene system is non-planar. However, 5-nitrofluorenone-4-carboxylic acid (IV) was not resolved by crystallisation of its morphine or quinidine salts, and this result can be interpreted

as indicating that the 4 : 5-positions of fluorene are farther apart than are the 6 : 6′-positions in a diphenic acid. This conclusion agrees with the fact that, although such systems as (VII) are readily formed, attempts to prepare compounds of type (VIII) have repeatedly failed (see Meyer, Meyer, and Taeger, *Ber.*, 1920, **53**, 2034).

(VII.)   (VIII.)

EXPERIMENTAL.

d- *and* l-6-*Nitrodiphenic Acids.*—The normal quinine salt of 6-nitrodiphenic acid was systematically crystallised from alcohol until it was separated into a slightly less soluble salt, $[\alpha]_{5461}$ + 286·6° ($c = 2·5$ in chloroform), and a slightly more soluble salt, $[\alpha]_{5461}$ − 122·4° ($c = 2·5$ in chloroform). The former on decomposition gave the *d*-acid with $[\alpha]_{5461}$ + 65·2° ($c = 3·01$ in ethyl alcohol), whilst the latter gave the *l*-acid with $[\alpha]_{5461}$ − 66·4° ($c = 4·91$ in ethyl alcohol). The *l*-acid had $[\alpha]_{5461}$ + 433° ($c = 4·69$ in 0·261*N*-sodium hydroxide), whilst the *d*-acid, obtained from its morphine salt, had $[\alpha]_{5461}$ − 434° ($c = 4·73$ in 0·426*N*-sodium hydroxide).

The solution of the sodium salt was kept at room temperature, and the following observations were made:

Time (days)	0	2	9	23	36·5	51
α_{5461}	−20·51°	−18·61°	−14·42°	−8·23°	−4·00°	−1·50°

Solutions of *d*-6-nitrodiphenic acid (1 g.) in 10 c.c. of acetic acid and in 10 c.c. of acetic anhydride were boiled under similar conditions for 1 hour, and they then had α_{5461} + 11·55° and 0·0° respectively ($l = 2$). After the acetic acid solution had been boiled for a further period of 5 hours, it had α_{5461} + 0·94°.

d-6-Nitrodiphenic acid (1 g.) was converted into 5-nitrofluorenone-4-carboxylic acid (see below). The acid obtained was inactive ($c = 2·4$; $l = 2$).

l-6-Nitrodiphenic acid was dissolved in excess of thionyl chloride and the solution evaporated in a vacuum. The residue was crystallised from benzene–light petroleum and gave the *l* + *dl*-acid dichloride, m. p. 65—68°, $[\alpha]_{5461}$ − 209·5° ($c = 5·04$; $l = 2$), whilst the mother-liquor on evaporation gave a further crop of the dichloride with $[\alpha]_{5461}$ − 220·6° ($c = 2·31$; $l = 2$ in chloroform).

d- *and* l + dl-4 : 4′ : 6 : 6′-*Tetranitrodiphenic Acids.*—Boiling alcoholic solutions of tetranitrodiphenic acid (35·7 g. in 1 l.) and

quinidine (30·5 g. in ½ l.) were mixed, and the precipitated salt was filtered off and boiled with alcohol until the residue attained constant rotatory power $[\alpha]_{5461}$ + 243·5° (c = 2·15 in 14·7N-acetic acid); m. p. 252° (decomp.). The alcoholic filtrates were evaporated, the residue was dissolved in acetic acid, and the resultant solution poured into dilute hydrochloric acid. The liberated tetranitrodiphenic acid was extracted with ether, and the well-washed extract dried with sodium sulphate and evaporated. The residue ($[\alpha]_{5461}$ *ca.* − 50°) was boiled with benzene, and the more soluble material was repeatedly crystallised from benzene until it attained constant rotatory power. *l* + *dl*-Tetranitrodiphenic acid formed needles which, after being heated at 130° for ½ hour, melted at 224—226° and had $[\alpha]_{5461}$ − 138·5° (c = 1·7 in ethyl alcohol). The less soluble quinidine salt was decomposed (*a*) by dissolving it in acetic acid and pouring the solution into dilute hydrochloric acid, (*b*) by dissolving in pyridine and pouring the solution into dilute ammonia, (*c*) by grinding with concentrated hydrochloric acid. The acids, recovered as described above and dried at 140°, had almost the same rotatory power, showing that racemisation does not occur during the recovery process.

d-4 : 4′ : 6 : 6′-Tetranitrodiphenic acid, m. p. 226—227° (Found : equiv., 211. Calc. : 211) (0·3696 g. in 20 c.c. of ethyl alcohol in a 2 dm. tube) gave :

λ	4359	4602	5461	5790	6708
α	+16·70°	+11·64°	+5·26°	+4·12°	+2·58°

whence $[\alpha]_{5461}$ +142·3°.

0·4209 G. in 20 c.c. of 1·033N/10-NaOH in a 2 dm. tube gave :

λ	4359	4602	5106	5218	5461
α	+29—31°	+19·6—20·0°	+10·84°	+9·72°	+8·00°
λ	5790	5896	6104	6708	
α	+6·33°	+5·86°	+5·08°	+3·78°	

whence $[\alpha]_{5461}$ + 190·5°.

After 39 days, this solution had α_{5461} + 8·08°.

A solution of *d*-tetranitrodiphenic acid in acetic anhydride (1 g. in 10 c.c.), with α_{5461} + 23·15°, had after 2 hours' boiling α_{5461} + 18·14°, and after 9 hours' boiling α_{5461} + 17·12°.

l-Tetranitrodiphenic acid was dissolved in thionyl chloride by boiling for 2 hours under reflux, and the solution was evaporated in a vacuum. The residue was difficultly soluble and melted indefinitely. Though no product was isolated in a pure condition, the optical activity was preserved, since $[\alpha]_{5461}$ − 133° (c = 2 in pyridine).

5-Nitrodiphenic acid was prepared by the process described by

Schmidt and Lumpp (*Ber.*, 1908, **41**, 4315). After 1 hour's boiling with acetic anhydride, the solution on cooling deposited crystals of *5-nitrodiphenic anhydride*, m. p. 193—195° (Found: C, 62·4; H, 2·9. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6%). 5-Nitrodiphenic acid (1·5 g.) in sulphuric acid (5 c.c.) was heated at 160° for ¼ hour, and after cooling poured into water. The precipitated *6(?)-nitrofluorenone-4-carboxylic acid* melted at 282° after crystallisation from acetic acid (Found: equiv., 270·5. $C_{14}H_7O_5N$ requires equiv., 269). 5-Nitrodiphenic acid gave non-crystallisable quinine, morphine, and quinidine salts. The brucine salt on crystallisation from water gave successive crops with $[\alpha]_{5461}$ — 10·4°, — 10·9°, — 11·2°, —11·1° ($c = 2·5$; $l = 2$ in 14·7*N*-acetic acid), indicating that no resolution had taken place.

5-Nitrofluorenone-4-carboxylic acid was prepared by the method of Moore and Huntress (*J. Amer. Chem. Soc.*, 1927, **49**, 1324). The quinidine salt showed slight irregularity in rotatory power ($[\alpha]_{5461}$ *ca.* — 20·6°; $c = 2·5$ in chloroform) but no resolution was effected. The morphine salt was crystallised from alcohol and showed a constant rotatory power of $[\alpha]_{5461}$ — 73·5° ($c = 2$ in 14·7*N*-acetic acid).

2 : 5 : 7(?)-*Trinitrofluorenone-4-carboxylic acid*, obtained by heating 5-nitrofluorenone-4-carboxylic acid (2·5 g.) with nitric acid (*d* 1·5; 50 c.c.) at 100° for 2 hours, pouring into water, and crystallising the resulting mass from aqueous alcohol, forms glistening, pale yellow plates, m. p. 254—255° (Found: C, 46·5; H, 1·7. $C_{14}H_5O_9N_3$ requires C, 46·8; H, 1·4%).

2 : 2′-Dinitrodiphenyl-4 : 4′-dicarboxylic acid was prepared from 4-bromo-3-nitrobenzoic acid. Its excessive insolubility militated against the production of uniform normal alkaloidal salts. The brucine salt on crystallisation from water varied in rotatory power between $[\alpha]_{5461}$ — 40° and $[\alpha]_{5461}$ — 56° ($c = 2$ in pyridine), but the liberated acid was inactive when observed in 1·033*N*/10-sodium hydroxide.

Quinine salts of 4-nitrodiphenic acid. An alcoholic solution of quinine (2 mols.) and 4-nitrodiphenic acid (1 mol.) was allowed to crystallise slowly. Successive crops had $[\alpha]_{5461}$ + 94·4°, + 84·0°, + 77·2° ($c = 2·5$ in chloroform), and the mother-liquor on evaporation and desiccation gave a solid with $[\alpha]_{5461}$ + 11·9°. Recrystallisation of the intermediate crops raised the rotatory power to $[\alpha]_{5461}$ + 106·4°; m. p. 180° (indefinite) (Found: C, 66·3; H, 5·6%). The liberated 4-nitrodiphenic acid was inactive in every case. The difference in rotatory power may be attributed to: (*a*) resolution of the alkaloidal salt; (*b*) admixture of acid and normal quinine salts and quinine; (*c*) differences in the number of

molecules of solvent of crystallisation—none of the salts lost more than 0·5% by weight on drying for 1 hour at 120°, however; or (*d*) possible presence of 6-nitro- and 4 : 4′-dinitro-diphenic acids as impurities.

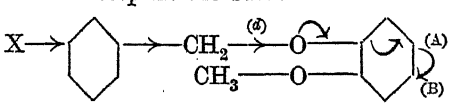
In conclusion, the authors wish to express their thanks to the Department of Scientific and Industrial Research for a grant made to one of them.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 6th,* 1927.]

CCXCIX.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR′N *in Aromatic Substitution. Part VI. The Nitration of* m- *and* p-*Chlorobenzyl Ethers of Guaiacol.*

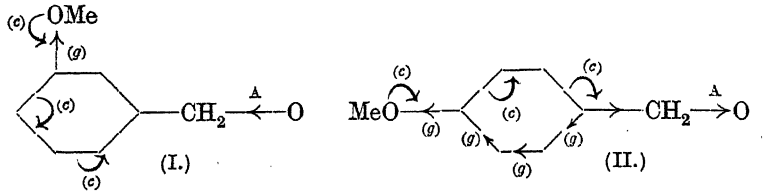
By ALBERT EDWARD OXFORD and ROBERT ROBINSON.

IN studying the relative directive powers of substituted benzyloxy-groups, we examine, in effect, the influence of the modified benzyl group on the electrons of the oxygen atom, and an important feature of the method is that the reactive centres are spatially removed from the benzyl group. The annexed diagram serves to illustrate this point, and just as Flürscheim secured a more just comparison of groups by excluding for certain purposes the ortho-derivatives, so we imagine that the device of relaying the effects of a group and estimating them at a distant point in the molecule constitutes a further step in the same direction.



In the case represented, X and also X·C_6H_4 are hypothetical kations that have a smaller electron affinity than a proton: this produces an electron displacement (*d*) in the sense indicated and relative to the mean positions of electrons in the corresponding position in the methoxy-group. The contiguous oxygen atom and the associated crotenoid system are thus stimulated, and the velocity of substitution at (B) is greater than that at (A). Groups are compared by putting them separately into competition with methoxyl, and in Part II (J., 1926, 383) it was shown in this way that the directive powers of the *m*-nitrobenzyloxy- and *p*-nitrobenzyloxy-groups are approximately equal (67; MeO = 100). Similarly, the directive power of the *m*-methoxybenzyloxy-group was found to be 92, indicating that in the absence of conjugative

disturbances, admittedly never completely eliminated in the formal systems, the methoxyl group must be regarded as one that has a greater electron affinity than hydrogen (I; resultant effect $g>c$ at A). Unfortunately, the directive power of the *p*-methoxybenzyloxy-group could not be determined; we had anticipated a considerably augmented value (>113, the directive power of the benzyloxy-group) as the result of the combined conjugative and general effect shown in (II) ($c>g$ at A).



The chlorine atom has a greater electron affinity than the methoxyl group, implying an increased general effect and a decreased conjugative effect, and the theoretical disparity between the directive powers of *m*- and *p*-chlorobenzyloxy-groups is thus smaller than that which should exist between the directive powers of the *m*- and *p*-methoxybenzyloxy-groups. Actually, we find that *m*-chlorobenzyloxy- has the directive power 69, and *p*-chlorobenzyloxy- 82. In both cases, therefore, the general effect of chlorine is paramount, but the higher value for the para-derivative is in harmony with our theoretical anticipations, and is probably due to crotenoid conjugation analogous to that symbolised in (II). The close approach of the directive power of *m*-chlorobenzyloxy- to that of *m*-nitrobenzyloxy-, showing that the electron affinity of chlorine is almost as strong as that of the nitro-group, need not occasion surprise, since the charges in the semi-polar double bonds, often assumed to be integral, are not really effective as such on account of the distortion and polarisation of the atoms that must enfeeble their external fields. It is probable that the difference between Cl and NO_2 lies not so much in their respective electron affinities as in the circumstance that Cl possesses free electrons, whereas the N of NO_2 does not. Therefore in C–Cl there may be occasional phases, non-existent in the case of C–NO_2, in which the co-valency with the carbon atom is increased, or alternatively, in which the electron density in the neighbourhood of the carbon atom is increased by the chlorine atom to such an extent that a co-valency change would occur if an electron-seat were available. The C–Cl group is thus the more plastic, and the electric intensity of the external fields varies over a greater range. This condition would be sufficient to account for such facts as the predominating *op-*

substitution of $Ph{\cdot}CH_2{\cdot}Cl$ as compared with the *mp*-substitution of $Ph{\cdot}CH_2{\cdot}NO_2$, even although the *average* electron affinities of Cl and NO_2 were approximately equal. The method of examination through a relay atom overcomes this difficulty to a large extent, because the phases at the C–Cl group that favour the reaction examined cannot be effective unless they happen to synchronise with a phase of the relay atom ($\overset{\curvearrowright}{O}$—C in the cases considered in this communication) also promoting reaction. It is obvious that this requirement must augment the relative importance of the normal conditions and diminish the magnitude of effects of the infrequent phases, $C\overset{\curvearrowleft}{—}Cl$ and $C\leftarrow\!\!—Cl$.

Experimental.

Shoesmith and Slater (J., 1926, 219) obtained *m*-chlorobenzyl bromide, b. p. 109°/10 mm., from *m*-nitrobenzaldehyde through *m*-chlorobenzaldehyde and *m*-chlorobenzyl alcohol, which was treated with hydrogen bromide in benzene solution. We have employed two methods: (*A*) Aceto-*p*-toluidide ⟶ 3-chloro-*p*-toluidine (Chattaway and Orton, J., 1900, **77**, 792) ⟶ 2-chloro-4-methylphenylhydrazine ⟶ *m*-chlorotoluene ⟶ *m*-chlorobenzyl bromide (by refluxing with the theoretical amount of bromine). (*B*) *m*-Nitrobenzyl alcohol ⟶ *m*-aminobenzyl alcohol (Lutter, *Ber.*, 1897, **30**, 1065) ⟶ *m*-chlorobenzyl alcohol (in excellent yield) ⟶ *m*-chlorobenzyl bromide (by means of bromine and red phosphorus, compare Part II, *loc. cit.*). Both processes yielded an oil, b. p. 120—123°/24—25 mm., and the specimens were identified by conversion into 5-nitro-2-*m*-chlorobenzyloxyanisole, m. p. 121°. A mixture of the two specimens melted at the same temperature.

p-Chlorobenzyl bromide was obtained by the bromination of *p*-chlorotoluene (44 g.) (Jackson and Field, *Ber.*, 1878, **11**, 905). After crystallisation from 85% alcohol, 15 g. of nearly colourless needles, m. p. 50°, were obtained (Shoesmith and Slater, *loc. cit.*, give m. p. 51°). The following guaiacol and nitroguaiacol ethers were prepared by methods closely resembling those employed previously (Part II, *loc. cit.*) for the corresponding *m*- and *p*-nitrobenzyloxy-derivatives. The crude products never melted more than 1° lower than the true m. p., but were recrystallised two or three times, a process which did not alter the m. p.'s.

2-m-*Chlorobenzyloxyanisole*, $MeO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$, b. p. 207—208°/15 mm., crystallised from light petroleum in slender needles, m. p. 46—47° (Found: C, 67·2; H, 5·4. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·3%). It is readily soluble in most organic solvents.

4-*Nitro*-2-m-*chlorobenzyloxyanisole*, $MeO{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$,

crystallises from alcohol in minute, slender, colourless needles, m. p. 129—130·5° (Found: Cl, 12·3. $C_{14}H_{12}O_4NCl$ requires Cl, 12·1%).

5-*Nitro*-2-m-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, feathery needles, m. p. 121° (Found: C, 57·0; H, 4·4. $C_{14}H_{12}O_4NCl$ requires C, 57·2; H, 4·1%).

2-p-*Chlorobenzyloxyanisole* crystallises from methyl alcohol in colourless, rectangular prisms, and from light petroleum in large, very well-defined prisms, m. p. 70° (Found: Cl, 14·3. $C_{14}H_{13}O_2Cl$ requires Cl, 14·3%). A description of these (Fig. 1) is contributed by Mr. H. E. Buckley, of the Crystallography Department of this University.

FIG. 1.

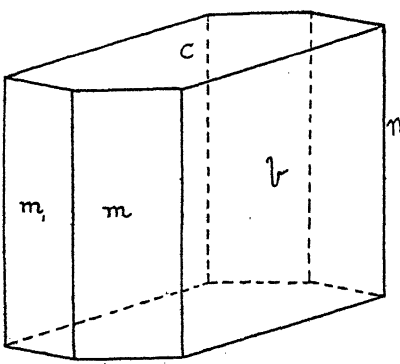
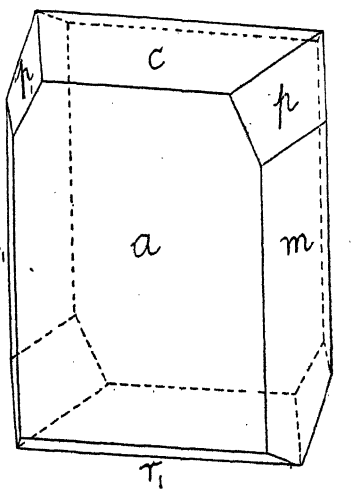


FIG. 2.



Symmetry: rhombic. Axial ratios: $a : b : c = 0{\cdot}7054 : 1 : 0{\cdot}7013$. Forms developed: b(010, tabular), c(001), m(110); (011) is very rare. Mean angular values: 011—001, 35° 3′ (6 angles; limits, 35° 0′—35° 12′); 010—110, 54° 48′ (24 angles; limits, 54° 35′—55° 1′). Cleavage: imperfect, parallel to 100.

4-*Nitro*-2-p-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, lustrous, feathery needles, m. p. 115—117° (Found: Cl, 11·8%).

5-*Nitro*-2-p-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, flat needles, m. p. 120—120·5° (Found: Cl, 12·0%). Mr. Buckley has kindly examined the crystals (Fig. 2) deposited on slow evaporation of a solution in light petroleum.

System: monoclinic prismatic. Axial ratios: $a : b : c = 2{\cdot}699 : 1 : 1{\cdot}708$. $\beta = 74°\ 40'$. Habit: somewhat tabular on a(100). Forms generally developed: a(100), m(110), $r(\bar{1}01)$, c(001),

and *p*(111). Mean angular values (calculated values in parentheses): *ac* 74° 40′, *am* 68° 59′, *ra* 69° 5′, *mc* 84° 37′ (84° 33′), *mr* 36° 15′ (36° 15′), *m* (110) *m*′ (1$\bar{1}$0) 42° 3′ (42° 3′), *pc* 56° 12′ (56° 1′).

Mixtures of 4- *and* 5-*Nitro*-2-m-*chlorobenzyloxyanisoles*.—The following freezing points were observed, the first number of each pair indicating the % of the 5-nitro-isomeride in the mixture: 15·36, 123·7° (1); 22·62, 119·85° (2); 30·42, 115·05° (3); 38·09, 110·0° (4); 43·12, 106·0° (5); 46·34, 103·65° (6).

Nitration of 2-m-*Chlorobenzyloxyanisole*.—The conditions given for the nitration of 2-*p*-nitrobenzyloxyanisole (Part II, *loc. cit.*, p. 389) were followed exactly. 1·7214 G. of the ether gave 2·0119 g. of the dried nitration product (yield, 99·0%), which was almost colourless and melted to a transparent liquid only slightly darker than that formed on fusion of the pure nitro-ethers. The filtrate and washings from the nitration were colourless and gave no coloration on the addition of sodium hydroxide. Since this product was found to behave as a binary mixture, it was not considered necessary to purify it by washing with methyl alcohol or in any other way. The f. p. of the nitration product was 107·55°, and from the graph we find: 5-nitro-isomeride, 41·1% [the Lagrange interpolation formula gave 41·3%, from points (2) to (5) inclusive]. A mixture of the nitration product (1·3779 g.) and the 4-nitro-isomeride (0·4796 g.) had f. p. 115·1°, practically coinciding with point (3) (30·42% of the 5-nitro-isomeride) and showing 40·9% of the 5-nitro-isomeride in the nitration product. A mixture of the nitration product (1·3779 g.) and the 4-nitro-isomeride (0·7884 g.) froze at 117·9° (5-nitro-isomeride, 25·95% from the graph), giving 40·8% of the 5-nitro-isomeride in the nitration product. A mixture of the 5-nitro-isomeride (0·6151 g., 41%) and of the 4-nitro-isomeride (0·8865 g.) froze at 107·8°, whilst the addition of 4-nitro-isomeride (0·5494 g.), reducing the 5-nitro-isomeride to 30·0%, raised the f. p. to 115·4°. These observations confirm those used in constructing the graph, and it appears that the nitration product contains 41% of the 5-nitro-isomeride. Hence the directive power of the *m*-chlorobenzyloxy-group is 69·5 (MeO = 100).

Mixtures of 4- *and* 5-*Nitro*-2-p-*chlorobenzyloxyanisoles*.—The following freezing points were observed, the first number of each pair indicating the % of the 5-nitro-isomeride in the mixture: 0, 116·3° (1); 9·8, 111·25° (2); 20·48, 106·0° (3); 32·26, 99·25° (4); 36·73, 95·6° (5); 44·86, 89·55° (6); 49·82, 84·8° (7). In (7) the first f. p. was 84·8°; the temperature then fell to 84·6°, and gradually rose to 86·05°, at which it remained constant for several minutes. This behaviour indicates the formation of an equimolecular compound of the components.

Nitration of 2-p-*Chlorobenzyloxyanisole.*—Except for the numerical details, the remarks made above on the *m*-isomeride are applicable to this case in every respect. (*a*) 1·9816 G. gave 2·3169 g. of the dried nitration product (yield, 99·0%) (Found : C, 57·1; H, 4·1. Calc. for $C_{14}H_{12}O_4NCl$: C, 57·2; H, 4·1%). (*b*) 1·2848 G. gave 1·4942 g. (yield, 98·5%). Nitration product (*a*) froze at 89·15°, (*b*) at 89·0°, and the f. p. 89·1° corresponds on the graph to 45·4% of the 5-nitro-isomeride. Mixtures of the nitration product (1·4424 g.) with the 4-nitro-isomeride (0·3487 g. and 0·6065 g.) had f. p.'s 96·0° and 99·55°, respectively. Both these values are very close to determined points (5 and 4 respectively) : the first corresponds to 36·24% of the 5-nitro-isomeride, giving 45·0% of this in the nitration product, and the second to 31·74% of the 5-nitro-isomeride, giving 44·8% in the nitration product. The f. p. of a mixture of the 5-nitro-isomeride (0·7226 g., 44·85%) and the 4-nitro-isomeride (0·8884 g.) was 89·2°. Hence the nitration product contains 45% of the 5-nitro-isomeride, and the directive power of the *p*-chlorobenzyloxy-group is 82 (MeO = 100).

THE UNIVERSITY, MANCHESTER. [*Received, July 20th,* 1927.]

CCC.—*The Thermal Dissociation of Carbonyl Chloride.*

By HORACE INGLESON.

THE object of the present work was to obtain satisfactory values for the dissociation constant of a chemical change. As carbonyl chloride dissociates at temperatures sufficiently low to admit of accurate determinations being made, it was decided to study this particular change. Reference to the literature showed serious differences in the results of investigators prior to 1921; these results are summarised in Table I. At the lower temperatures, the values are in bad agreement. Thus, an approximate calculation shows that the value at 341° obtained by extrapolation from Horak's data (Diss., Berlin, 1909) would be of the order of 4000, and not 8280 as calculated from the results of Atkinson, Heycock, and Pope (J., 1920, **117**, 1410). At the higher temperatures, there is a similar lack of agreement among different workers : in nearly every case the results of Atkinson, Heycock, and Pope correspond to a smaller degree of dissociation than that found by other workers.

Bodenstein and Dunant (*Z. physikal. Chem.*, 1908, **61**, 437) used the streaming method in their experiments, and determined the equilibrium both from the thermal combination of carbon monoxide and chlorine and from the dissociation of carbonyl chloride. They

concluded that their results confirmed the theory of Nernst as well as could be expected in the absence of values for the specific heat of carbonyl chloride. Horak (*loc. cit.*) used a quartz spiral manometer in order to measure the pressure developed in a heated porcelain tube filled with the gas, whereas Atkinson, Heycock, and Pope (*loc. cit.*) applied the streaming method to measure the extent of the thermal dissociation of the gas in the presence of a catalyst at temperatures between 101° and 517°.

During the progress of the present work, Christiansen (*Z. physikal. Chem.*, 1922, **103**, 99) published the results of an investigation of the factors affecting the velocity of decomposition of the gas at different temperatures. He concluded that the decomposition was accelerated by the chlorine produced, but his work gives very little information concerning the dissociation constants.

In 1924, Bodenstein and Plaut (*Z. physikal. Chem.*, **110**, 399) described experiments made at temperatures between 373° and 451°, and their results are included in Table I. They were able to confirm the observation of Christiansen that the chlorine accelerates the decomposition.

TABLE I.

Data at present available.

Temp.	K_c.	Author.*	Temp.	K_c.	Author.*	Temp.	K_c.	Author.*
603°	15·0	B.D.	460°	298·7	A.H.P.	404°	1123·0	H.
553	38·0	B.D.	451·3	264·8	B.P.	400	954·6	A.H.P.
506	612·5	A.H.P.	450	343·9	H.	399	1365·0	H.
505	379·0	A.H.P.	449	425·0	A.H.P.	394·6	1230·0	B.P.
505	105·4	A.H.P.	444·1	348·2	I.	389	1409·0	I.
503	78·2	B.D.	443	419·1	A.H.P.	384	2054·0	H.
500	137·5	H.	425	630·7	H.	373·3	1884·0	B.P.
486	209·5	A.H.P.	415	717·9	I.	357	3654·0	I.
481·4	151·6	I.	413·6	719·5	B.P.	341	8281·0	A.H.P.
475	223·9	H.	406	1414·0	A.H.P.			

* B.D. Bodenstein and Dunant. A.H.P. Atkinson, Heycock, and Pope. B.P. Bodenstein and Plaut. I. Ingleson (present paper). H. Horak.

Preliminary Experiments at the Boiling Point of Sulphur.

1. *Chemical Series.*—From a consideration of the difficulties inherent in the streaming method, it seemed likely that some modification of the static method would be more suitable for carrying out the experiments. In the first series of eight experiments, which gave a mean value of $K_c = 354$, a known weight of carbonyl chloride was heated in a closed, thin-walled bulb of glass by suspending it in the vapour of sulphur boiling under atmospheric pressure. At the end of 8 hours, the bulb was quickly removed from the heating bath into a rapid current of carbon dioxide; it was shielded from the light, and the chlorine was determined iodometrically.

This series of experiments and later series in which a similar method was used have been called " chemical." It was decided to control these results by a second set of experiments at the same temperature, based on methods which may be termed " physical."

2. *Physical Series.*—In this series, a glass bulb, filled with a known amount of carbonyl chloride, was heated as before, but the pressure corresponding to equilibrium was measured in a manometer containing mercury after the interposition of an " air buffer." This series gave the value $K_c = 364$ as the mean of eight experiments. Since the agreement of the results of the two series at the boiling point of sulphur was satisfactory, the methods were applied at the boiling point of mercury.

Preliminary Experiments at the Boiling Point of Mercury.

1. *Physical Series.*—The experiments were carried out in the manner just described except that a small amount of charcoal was used to accelerate the rate of attainment of equilibrium. The mean of four concordant results was $K_c = 3007$.

2. *Chemical Series.*—On account of the small extent of decomposition, the chlorine determinations were checked by making careful measurements of the amount of carbon monoxide formed. It was found that the percentage decomposition calculated from the determination of the chlorine was smaller in every instance than that derived from the carbon monoxide measurements; *e.g.*, in one experiment the carbon monoxide measurements indicated 9·1% decomposition (corresponding to $K_c = 3249$), whilst 7·8% decomposition ($K_c = 4429$) was calculated from the chlorine determinations. The means of the values from the chlorine and carbon monoxide determinations were, respectively, $K_c = 4350$ and $K_c = 3181$. It will be seen that the value obtained in the physical experiments, $K_c = 3007$, agrees better with the latter than with the former. As it was clear that the chemical method could not be used with advantage, the physical method was modified so that continuous observation of the pressure of the decomposing gas could be made. By this means, it was found possible to establish the cause of the discrepancy between the two sets of results.

3. *Second Physical Series.*—The apparatus used consisted of a reaction vessel of glass which was joined to a U-tube containing concentrated sulphuric acid. By suitable manipulation of a tap, the U-tube could be made to serve as a manometer which protected the mercury in a second manometer from attack by the chlorine produced in the decomposition. The reaction vessel was filled with carbonyl chloride at room temperature to a convenient pressure, and after the heating of the vapour-bath had commenced, the

levels of the acid in the U-tube were maintained nearly constant by gradually increasing the pressure of the air in one limb of the tube. Readings of the pressure of the gases in the bulb were made at regular intervals after the temperature of the bath became constant. It was expected that the pressure would gradually increase to a constant value, the rate of increase slowly falling to zero. It was found, however, that the rate of increase of pressure did not fall to zero, but only decreased to a small constant value even after prolonged heating had taken place. This suggested that the observed rate of change was not determined simply by the dissociation of carbonyl chloride. On removing the bulb from the heating bath, a marked etching of the inner surface was noticed. The white solid which gave the etched appearance showed the reactions of a chloride.

The results of the eight experiments comprising this series gave an average value of $K_c = 3031$, which is in good accord with the results from the chemical determinations of the carbon monoxide ($K_c = 3181$) and from the first physical series ($K_c = 3007$). These three results lend support to the following explanation of the non-equivalence of the chlorine and carbon monoxide in the chemical series. During the prolonged heating, the materials of the bulb were attacked by the chlorine present and evolution of gas took place. The removal of the chlorine caused a disturbance of the equilibrium and further dissociation of carbonyl chloride took place to re-establish it. Thus, analysis by the chemical method gives a quantity of free chlorine which is too small, whilst the amount of gas determined as carbon monoxide is too large. From this it may be concluded that trustworthy results cannot be obtained in experiments in which the gases are heated for long periods in glass bulbs. A bulb of transparent fused quartz was therefore employed in the later experiments.

Later Experiments.

The results obtained in the five series of experiments made at 357°, 389°, 415°, 444·1°, and 481·4° have been summarised in Table I. Experiments were first made in vapour baths at 357° and 444·1°; subsequent experiments were precisely similar except that they were carried out in an electric furnace. Those at 389° and 415° were chosen so as to give nearly equal intervals, and when the results at these four temperatures were plotted it was found that a straight line passing through the points corresponding with 357°, 415°, and 444·1° did not pass exactly through that corresponding with 389°. Further experiments were made at 481·4°, which clearly showed that a straight-line relationship exists between

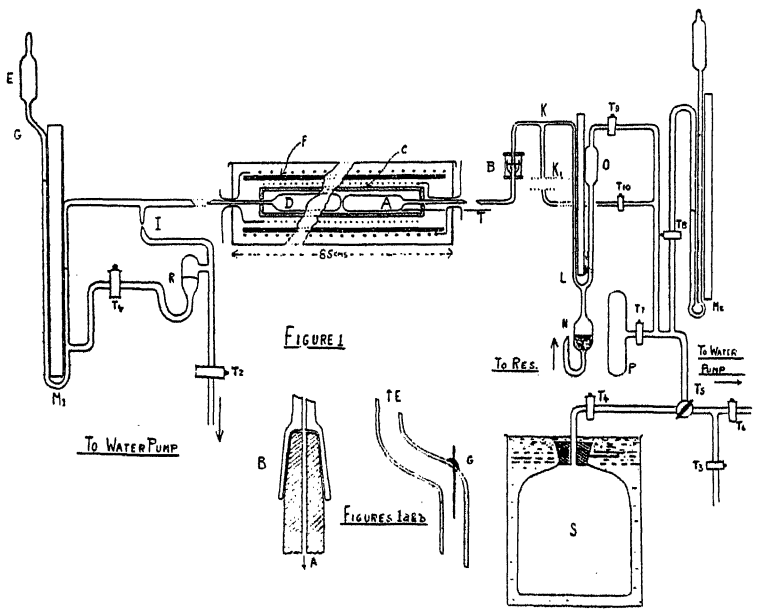
the reciprocals of the temperature and the logarithms of the constants.

Experimental.

The phosgene used throughout was obtained from Kahlbaum in sealed glass bombs. The apparatus is shown in Fig. 1. The quartz bulb, A, had a capacity of about 175 c.c. and was placed inside the heavy copper tube, C. It was joined to the rest of the apparatus through the ground joint, B. This was specially made in order to contain the smallest possible volume (see Fig. 1A), and was lubricated with a thin layer of chlorinated lanoline from which all traces of volatile substances had been removed. The whole was sealed by immersion in mercury, and the two sections of the joint were securely held together. The copper tube was about 65 cm. in length and 5·4 cm. in diameter, and had a wall thickness of 9 mm. Thick copper plates were fixed to the ends of the tube after the bulbs A and D had been placed in position. The tube was evenly wound with heavy gauge nickel-chrome wire, the winding being carried as near to the ends of the tube as possible. The tube F extended beyond the ends of the copper tube for a length of about 8 cm. It reduced the loss of heat from the ends of the copper tube and also kept this tube in an enclosure at a fairly uniform temperature. The tubes were carefully packed in kieselguhr in an iron box. The bulb D was of glass and had a capacity of about 500 c.c. The manometer M_1 carried an evacuated bulb, E, and had a stout platinum wire fused in at G (see Fig. 1B). The T-piece, I, served only in the drying and filling of the bulb, D. The portion of the apparatus just described is called the air-regulator. It served as an air thermometer and also controlled the current supplied to the furnace. The windings round the iron and copper tubes were in parallel and the circuits were so arranged that when that round the copper tube was broken by the operation of the air-regulator, about 2% of the total current was cut off. Fluctuations in the total current caused by changes in the voltage at the laboratory mains were compensated for by the adjustment of a rheostat by hand. This regulation of the current was carried out continuously during the whole time required for an experiment. Observations showed that it was easy to maintain the temperature constant to $\pm 0{\cdot}25°$ when the temperature of the laboratory was kept fairly constant. The pressure of the carbonyl chloride at room temperature is shown in Tables II and III under the heading p_1. After the pressure of the air in the large bottle, S, had been adjusted to be nearly equal to p_1, the tap, T_4, was closed. The bottle was kept in a well-regulated thermostat. The quartz bulb and all the connecting tubes were repeatedly evacuated and washed

out with the gas before being filled. Air-free, concentrated sulphuric acid was allowed to close the seal, L, and enter O to a convenient height. The pressure of the gas in the quartz bulb was measured on the vacuum-type manometer, M_2. The heights of the mercury in the manometers were read to 0·1 mm. with the aid of a cathetometer. The temperature of the gas was read on a mercury thermometer, T, graduated to 0·1°, which had been checked at the melting point of ice and at the transition point of the system $Na_2CrO_4,10H_2O$–$Na_2CrO_4,6H_2O$–H_2O. After the pressure and temperature of the air in the bulb D had been measured, a nitrogen-filled

FIG. 1.



thermometer was put in position, the tap T_4 was opened and the heating current passed through the furnace. Well-dried air was admitted into S to keep the levels of the acid in the seal nearly stationary and thus compensate for the gradual increase in pressure of the gases in the quartz bulb. During the heating, approximate measurements were made of the pressures of the gases in the bulbs. It was observed that up to about 350° the pressures increased roughly in proportion to their initial values. Then the gases in the quartz bulb began to exert a proportionately greater pressure than did the air in the bulb D. This effect became more and more marked, and the rate of decomposition as deduced from pressure measurements passed through a maximum value after the highest temperature

had been reached. This behaviour is in accord with the observations of Christiansen (*loc. cit.*). When the pressure of the decomposing gas ceased to increase, the experiment was discontinued. Heating of the bulb was in all cases continued for 12—24 hours after chemical equilibrium appeared to have been reached. The pressures corresponding to equilibrium are given in Tables II and III in columns headed p_2.

In order to provide a check upon the high temperatures employed, air was frequently substituted for carbonyl chloride in the bulb A. Measurements of the quantity pv/T for the quartz bulb and the tubing connected to it were made. The value of T at the high temperature was deduced from measurements of the pressures in the air-regulator. As an example of the values found at the low and high temperatures, a determination at 389° is given: pv/T at 19·2° = 157·7; pv/T at 389° = 157·5.

In determining the true value of the concentrations of the gases composing the equilibrium mixture, several corrections were introduced. A small amount of carbonyl chloride in the tubing between the furnace and the meniscus of the acid in the seal was exposed either to bright daylight or to an electric lamp, and thus was not at the temperature of the furnace when the final pressure measurements were made. It is evident that if the equilibrium mixture of gases in the hot bulb could be separated from the gas in the cold tubing and then allowed to regain its original composition and temperature of filling, it would not exert a pressure p_1, but a smaller pressure.

The separate series of experiments which gave the mean values shown in Table I are discussed below.

TABLE II.

Results obtained at the boiling point of mercury.

No.	p_1 (mm.).	Temp.	p_2 (mm.).	% Dec.	K_c (corr.).	B. p. (°K.)
19	304·57	16·8°	737·66	12·32	3470	629·2°
20	292·78	14·7	712·8	12·92	3778	629·5
21	305·46	15·2	741·3	11·47	3813	630·1
22	301·44	15·3	732·46	11·89	3766	630·9
23	291·25	14·3	714·0	12·24	3633	630·5
24	299·59	20·6	717·9	12·22	3608	629·6
25	304·77	20·6	730·25	12·30	3512	630·25
					Mean 3654	

Table II gives the results of experiments made at the boiling point of mercury; the alteration of the boiling point with the change n the atmospheric pressure was taken into account. (Data for this correction, and also for that of the series at the b. p. of sulphur, are taken from the *Chemiker Kalender*, 1922, Vol. 2, pp.

129, 130.) The temperature at which each experiment was made is shown in the last column of the table.

It is considered that the results are more trustworthy than any hitherto obtained at 357°. The values of the constant are calculated directly from the percentage decomposition (% Dec.) after the use of the corrections referred to above.

TABLE III.

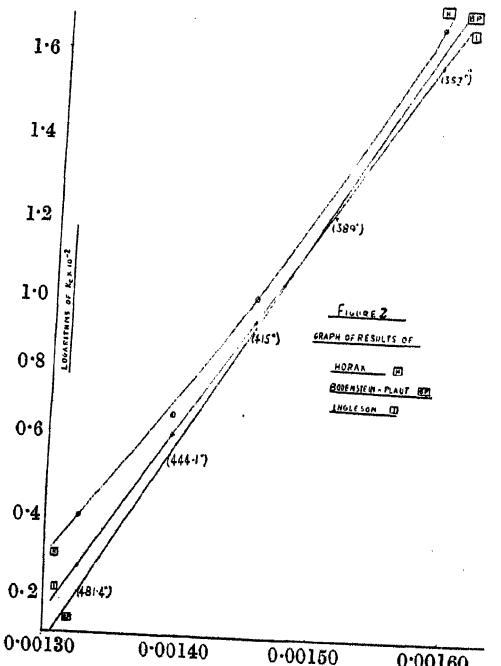
No.	p_1 (mm.).	Temp.	p_2 (mm.).	% Dec.	K_c (corr.).
	(*a*) Results obtained at 388—389°.				
1	271·27	14·9°	748·36	20·55	1248
2	259·5	11·6	722·80	20·36	1319
3	276·34	21·4	747·77	20·46	1118
4	268·89	20·4	729·30	20·63	1273
5	248·23	21·7	667·27	20·34	1432
7	259·87	21·1	703·10	20·56	1352
8	250·76	19·3	680·22	20·22	1423
9	246·06	23·05	662·32	20·79	1373
	(*b*) Results obtained at 415°.				
1	244·80	14·5°	743·10	27·27	720·0
2	231·15	12·6	708·38	27·84	722·1
3	232·20	12·7	710·62	27·71	726·3
4	232·30	12·5	712·90	27·99	707·1
5	231·61	10·5	714·65	27·86	714·0
				Mean	717·9
	(*c*) Results at the b. p. of sulphur (average temp., 444·1°).				
1	206·80	23·6°	692·15	39·14	357·9
2	196·43	18·4	672·03	40·21	345·2
3	203·43	19·3	691·22	39·57	349·6
4	204·22	21·0	687·14	39·48	353·1
5	203·50	16·8	697·08	39·71	343·7
6	204·28	16·0	706·71	41·38	307·5
7	204·20	16·9	698·01	39·26	353·0
8	210·56	15·7	721·04	39·56	335·1
				Mean	348·2
	(*d*) Results at 480·3°, 481·2°, and 482·5°, respectively.				
1	203·25	21·1°	788·41	52·31	158·2
2	184·78	20·2	729·75	54·40	153·5
3	187·00	17·35	751·93	55·22	143·2
				Mean	151·6

Of the experiments in Table III*a*, Nos. 1—4 were made at 388° and the others at 389°. The mean from Expts. 5—9 is $K_c = 1395$, or, excluding No. 7, $K_c = 1409$. It was found that a trace of sulphuric acid had entered the quartz bulb in Expts. 1—4; the effect of this would be to give too large a final reading of the pressure p_2 and thus too small a value for K_c. Furthermore, since the value $K_c = 1409$, from Expts. 5, 8, and 9, approximates more closely to the smoothed curve representing the results at other temperatures (see p. 2252), this value is regarded as the more trustworthy and is quoted in Table I.

A comparison of the results given in Table IIIc (which all relate to temperatures between 443·7° and 444·8°) with the values obtained in the preliminary experiments at the boiling point of sulphur shows a very satisfactory agreement between the three sets of values.

In the graph shown in Fig. 2 the values of log $K_c/100$ have been plotted against the reciprocals of the corresponding absolute temperatures, the Centigrade temperatures being shown along the

FIG. 2.



Reciprocals of absolute temperature.

course of the graph. The values now found are seen to be approximately intermediate between the most satisfactory values hitherto published. When plotted on a scale sufficiently large to take account of 0·0025 in the logarithms and of 5×10^{-7} in the reciprocals of the temperatures, the points corresponding to the temperatures 481·4°, 444·1°, 415·0°, and 357·0° lie exactly on a straight line. The value of K_c at 389° interpolated from this line is 1429, whereas the experimentally determined value is 1409, *i.e.*, about 1% smaller. There is little doubt that the curves of Horak and of Bodenstein and Plaut point to a value of the constant at 357° which is too

large. It is considered that the author's graph reproduces the values of the constant over a range of 120° with considerable accuracy.

Heat of Reaction.

Thomsen (" Thermochemische Untersuchungen," Vol. II, p. 359), in repeating the work of Berthelot on the heat of the reaction $CO + Cl_2 = COCl_2$, measured both (1) the heat change which occurs when carbonyl chloride is passed into aqueous potassium hydroxide, and (2) the heat evolved by the combustion of a mixture of the gas with hydrogen in an atmosphere of oxygen. Berthelot had used the first method and found a value of 18,000 cals., but Thomsen showed that the true value was much higher and obtained results of 26,620 and 25,650 cals. by the two methods. There is thus a difference of 970 cals. between the values given by Thomsen, the mean being 26,100 cals.

The results now obtained have been used to calculate this heat of reaction (Q_v), which has been assumed to remain constant within each temperature-range shown in Table IV. The range (4*a*) has been included to show the effect upon Q_v and Q_p of using the interpolated value (1429) of K_c at 662° K. instead of the experimental result (1409), which gives the results in range (4). Since Thomsen's data apply at constant pressure at room temperature, the comparison of his results must be made with those shown in col. 3 which are the heats of reaction at constant pressure at the mean temperatures shown in col. 4. The mean of these is 25,500 cals. at an average temperature of 416°, thus differing from Thomsen's mean by 600 cals.

TABLE IV.

Temp. ranges (°K.).	Q_v.	Q_p.	Mean temp., °K.
(1) 754·4—717·1	24,030	25,500	735·7
(2) 717·1—688	24,530	25,930	702·6
(3) 688—630	24,340	25,660	659
(4) 688—662	23,620	24,970	675
(4*a*) 688—662	24,100	25,450	675

It appears doubtful whether this difference between the two values has any real significance as it is within the limits of experimental error in Thomsen's results.

Summary.

The values found by different authors for the dissociation constant of carbonyl chloride show wide divergences, and experiments have therefore been made over a range of 120°—from 360° to 480°. It has been shown that trustworthy results cannot be obtained in experiments in which carbonyl chloride is heated in glass reaction

vessels for long periods. The results obtained in quartz vessels agree fairly well with those of Bodenstein and Plaut.

The values of the logarithms of the constants when plotted against the reciprocals of the absolute temperatures lie on a straight line.

Values calculated for the heat of the reaction show that this changes by an amount less than the uncertainty in Thomsen's values when measured at room temperature and at temperatures between 300° and 500°.

These facts lead to the conclusion that the difference between the sum of the molar heats of carbon monoxide and chlorine and that of carbonyl chloride is constant up to 500°, and that its numerical value is small.

Qualitative evidence was obtained in support of the observations of Christiansen that the decomposition of carbonyl chloride is catalysed by the products of decomposition.

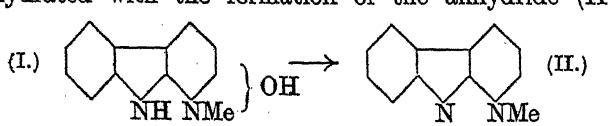
The author wishes to express his thanks to Mr. D. L. Chapman and Mr. H. J. George for the help and criticism which they have given during the course of the work. He is also indebted to the Department of Scientific and Industrial Research for a grant which enabled him to undertake the work.

THE SIR LEOLINE JENKINS LABORATORIES,
JESUS COLLEGE, OXFORD. [*Received, June 15th,* 1927.]

CCCI.—*Polynuclear Heterocyclic Aromatic Types. Part III. Pyrroloquinoline Derivatives.*

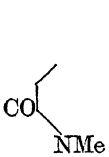
By REGINALD CLIFFORD FAWCETT and ROBERT ROBINSON.

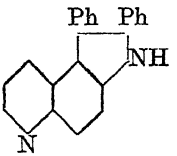
IN Part II of this series (Armit and Robinson, J., 1925, **127**, 1604) several anhydronium bases of the carboline type were described, and 3-carboline methohydroxide (I), for example, was shown to be dehydrated with the formation of the anhydride (II). An

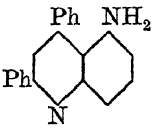


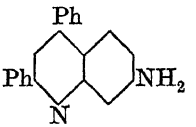
attempt was made to reproduce this phenomenon in the case of a base in which the pyridine and pyrrole rings were separated by a naphthalene nucleus, but without definite result; we have now made similar trials with compounds in which the separation of the heterocyclic nuclei is by a benzene nucleus. A study of the literature showed that the particular combinations of fused

rings which we wished to examine are not contained in known substances, and some difficulty has been experienced in effecting the necessary syntheses. 6-Aminoquinoline and benzoin (compare Japp and Murray, J., 1894, **65**, 889) could be condensed with formation of a *diphenylpyrroloquinoline* (III), but the *methosulphate* of this base, on treatment with aqueous potassium hydroxide, does not appear to yield an anhydro-base. It was thought that less ambiguous results would be obtained if the quinoline ring were

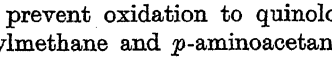

(IIIA.)

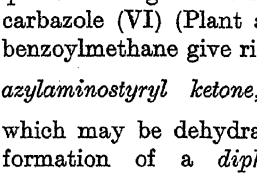

(III.)

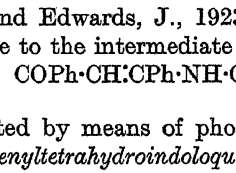

(IV.)

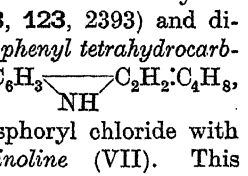

(V.)

phenylated in positions 2 and 4 in order to stabilise the α- and γ-carbinols and thus prevent oxidation to quinolones. The condensation of dibenzoylmethane and *p*-aminoacetanilide could not, however, be effected. With *m*-phenylenediamine the isomeric *aminodiphenylquinolines* (IV, V) were obtained, although in such poor yield that further work along these lines was prohibited.

We therefore turned our attention to a scheme in which the quinoline ring is the last to be introduced. 6-Aminotetrahydrocarbazole (VI) (Plant and Edwards, J., 1923, **123**, 2393) and dibenzoylmethane give rise to the intermediate *phenyl tetrahydrocarbazylaminostyryl ketone*,  , which may be dehydrated by means of phosphoryl chloride with formation of a *diphenyltetrahydroindoloquinoline* (VII). This


(VI.)

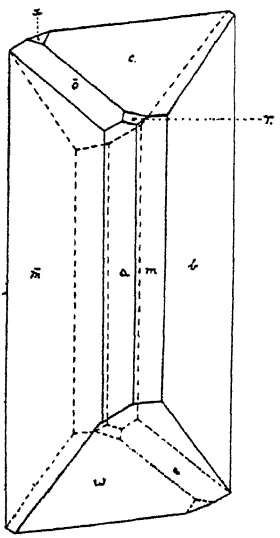

(VII.)


(VIII.)

yellow base gives red salts, and when dissolved in organic solvents it absorbs a molecular proportion of oxygen so as to produce a *dioxy-compound*, $C_{27}H_{22}O_2N_2$. The *substance* derived from the *methosulphate* of (VII) by the action of aqueous potassium hydroxide has, apparently, the composition $C_{28}H_{24}N_2,2H_2O$. In view of its deep green colour and the avidity which it displays for oxygen, it is better regarded as a hydrate of the anhydro-base (VIII) than

of the methohydroxide of (VII) (which should be red, like the methosulphate). Probably the most satisfactory conception of the nature of these intensely-coloured, hydrated anhydro-bases, several of which have now been found to exist, is that which would class them with the pyranhydrones and flavanhydrones as quinhydrones. Thus the substance under discussion would, on this hypothesis, have the composition, $C_{28}H_{24}N_2,C_{28}H_{26}N_2O,3H_2O$. The first component would be the fractional dipolar anhydronium base (compare Part II, *loc. cit.*), whilst the second would be a partly dissociated carbinol-amine, also a fractional dipole, balancing the first and cohering to it through electrostatic attraction. Such a conception of the molecular combination seems to be generally applicable to the quinhydrones.

FIG. 1.



EXPERIMENTAL.

5 : 6 - (2′ : 3′ - *Diphenylpyrrolo*)(4′ : 5′) - *quinoline* (III).—This base may be obtained from *p*-nitroaniline in an over-all yield of 43%, the yield in the last stage described below being 95%. A mixture of 6-aminoquinoline (7 g.), its hydrochloride (3 g.), and benzoin (15·5 g.) was heated for 4 hours at 150—160°. On cooling, the mass set to a hard cake which was ground with aqueous ammonia, and the yellow powder collected, washed, dried, and crystallised from methyl alcohol and then from ethyl acetate ; short, yellow prisms (19 g.), m. p. 167—168° (Found, in material dried at 100° : C, 81·4; H, 5·4; in material dried at 140° in a high vacuum : C, 86·0; H, 5·3. $C_{23}H_{16}N_2,H_2O$ requires C, 81·6; H, 5·3; $C_{23}H_{16}N_2$ requires C, 86·2; H, 5·0%). The molecule of water is tenaciously held and only removed very slowly at 110—120° in a vacuum. Solutions of the substance in most organic solvents are yellow and exhibit a green fluorescence.

A sample of this base was crystallised from ethyl acetate, and the following crystallographic description was kindly supplied by Mr. H. E. Buckley, of the Crystallography Department of this University :

Symmetry : anorthic, pinacoidal. Habit : short prisms, parallel to zone (001). Forms developed : $a(100)$, $b(010)$, $c(001)$, $m(110)$, $\bar{m}(1\bar{1}0)$, $o(1\bar{1}1)$, $w(11\bar{1})$, $r(101)$, $x(0\bar{1}3)$.

Table of Observed Angles.

Faces.	Angle.	No. of measurements.	Limits.
(010—$\bar{1}$10)	59° 41′	11	59° 20′—59° 56′
(100—110)	47° 50′	3	47° 45′—47° 57′
(100—1$\bar{1}$0)	33° 7′	5	33° 0′ —33° 13′
(110—010)	39° 28′	2	39° 28′ (each)
(001—010)	74° 51′	8	74° 35′—75° 3′
(001—$\bar{1}$10)	95° 56′	5	95° 46′—96° 6′
(001—1$\bar{1}$1)	42° 0′	7	41° 42′—42° 11′
(1$\bar{1}$1—1$\bar{1}$0)	42° 2′	6	41° 46′—42° 8′
(010—1$\bar{1}$1)	54° 13′	6	54° 5′ —54° 23′
(110—1$\bar{1}$1)	43° 13′	3	43° 4′ —43° 18′
(00$\bar{1}$—11$\bar{1}$)	69° 1′	6	68° 51′—69° 10′
(001—0$\bar{1}$3)	17° 29′	1	17° 29′

Axial angles: $a = 80° 37′$; $\beta = 70° 8′$; $\gamma = 77° 3′$.
$a : b : c = 0{\cdot}601 : 1 : 0{\cdot}530$.

Optics. When the crystal is laid on face $\overline{m}(1\bar{1}0)$, which is usually the largest face, there is an extinction, in parallel polarised light, practically parallel to the edge given by the $c(001)$ face and the prism. From observations in convergent polarised light, it appears that the birefringence is very strong and positive, whilst the dispersion appears to be of the type $\rho > \nu$.

The *hydrogen sulphate* and the *hydrochloride* crystallise from water and from dilute hydrochloric acid respectively in stellar clusters of pale yellow plates. The solution in concentrated sulphuric acid is both colourless and non-fluorescent. The *picrate* crystallises from alcohol in bright yellow needles, m. p. 218° (decomp.).

The Methosulphate.—Pure methyl sulphate (4 g.) in dry benzene (10 c.c.) was added to a solution of diphenylpyrroloquinoline (5 g.) in hot dry benzene (100 c.c.), and the mixture boiled. Bright yellow needles soon appeared and in 10 minutes filled the liquid. The salt was isolated and crystallised from water in yellow needles (5 g.), m. p. 218—219° (Found: S, 7·1. $C_{25}H_{22}O_4N_2S$ requires S, 7·2%). The orange-yellow, alcoholic solution exhibits a faint fluorescence, but the light yellow acetic acid solution has a vivid light green fluorescence. The colourless solution in concentrated sulphuric acid is not fluorescent, but on the addition of water the yellow colour and green fluorescence appear. The solubility in water is approximately: at 25°, 1 part in 70 parts; at 95°, 1 part in 7 parts. Decomposition of this methosulphate with 50% aqueous potash yielded an amorphous red powder.

2-Keto-1-methyl-5 : 6-(2′ : 3′-diphenylpyrrolo)(4′ : 5′)-1 : 2-dihydroquinoline (III, modified as in IIIA).—A cold concentrated aqueous solution of the above methosulphate (4 g.) was added to a 10% sodium hydroxide solution (50 c.c.) containing potassium ferri-

cyanide (5·9 g.), and the mixture was kept for an hour and frequently shaken. The product was isolated by means of ether and then extracted with boiling light petroleum; the solutions on concentration to a small volume deposited a pale yellow powder. The *quinolone* crystallised from ether in pale yellow needles, m. p. 195·5° (Found: C, 78·8; H, 5·2. $C_{24}H_{18}ON_2,H_2O$ requires C, 78·3; H, 5·4%); it is readily soluble in most organic solvents.

5- *and* 7-*Amino*-2 : 4-*diphenylquinoline* (IV, V).—*p*-Aminoacetanilide condenses with dibenzoylmethane to an anil, but ring closure of this could not be effected under a variety of conditions. The action of sulphuric acid on the anil, followed by treatment with aqueous sodium hydroxide gave a *substance*, m. p. 237·5—238·5°, crystallising from alcohol. This appeared to be the sodium salt of a sulphonic acid of the required base. 70% Sulphuric acid and also zinc chloride gave no useful results. We therefore directed our attention to *m*-phenylenediamine derivatives, but here too the experiments met with little success, since the yields of the desired aminodiphenylquinolines were only 5%. A mixture of *m*-phenylenediamine (6 g.) and dibenzoylmethane (12 g.) was heated at 140° for 1 hour; powdered zinc chloride (10 g.) was then introduced, and the temperature maintained at 175—180° for 5 hours. The bases produced were rendered to benzene, and the dried extract on concentration and keeping deposited a mixture of short, thick, prismatic needles and fine, silky needles. These were separated, and after many crystallisations from alcohol and benzene the two forms were obtained pure, their m. p.'s not being altered by further crystallisation; the former variety had m. p. 168·5° (Found: C, 85·0; H, 5·5%), and the latter had m. p. 187° (Found: C, 84·5; H, 5·8. $C_{21}H_{16}N_2$ requires C, 85·1; H, 5·4%); by analogy with other 5- and 7-substituted quinoline derivatives, the substance, m. p. 168·5°, should be the 5-substituted isomeride. The yellow colour of the base, m. p. 187°, is the paler of the two, but in other respects the properties of these substances are closely similar; a mixture had m. p. 142°. The bases may be diazotised, and then couple with β-naphthol to give bright red azo-compounds.

6-*Amino*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (VI).—*p*-Nitrophenylhydrazine (the method of Hodgson and Beard, *J. Soc. Chem. Ind.*, 1926, **45**, 56T, gives almost theoretical yields) was converted into 6-nitrotetrahydrocarbazole, as described by Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 53) (yield, 80%), but the recorded processes for the reduction of this substance (compare Perkin and Plant, J., 1921, **119**, 1833; Plant and Edwards, *loc. cit.*) gave only 20—40% yields. The use of sodium sulphide as the reducing agent led to still lower results, but a 73% yield was obtained by

means of iron powder and hydrochloric acid in alcoholic solution (compare West, J., 1925, **127**, 494). 6-Nitrotetrahydrocarbazole (20 g.), dissolved in boiling 90% alcohol (70 c.c.) (reflux condenser, mechanical stirrer, and wide, stoppered side-tube) and concentrated hydrochloric acid (1 c.c.), was reduced by the gradual addition of iron powder (24 g.) during 45 minutes and subsequent boiling for 3—4 hours. The mixture was filtered hot and the residue washed with boiling alcohol; the amine (12·5 g.) was isolated from the filtrate by precipitating neutral impurities with concentrated hydrochloric acid (50 c.c.) and separating the hydrochloride by the further addition of hydrochloric acid (100 c.c.). Extraction of the neutral substances by water yielded some more amine hydrochloride, and the final acid mother-liquor was concentrated, basified with ammonia and the crude base crystallised from water.

Phenyl α-Tetrahydrocarbazylamino(6)*-styryl Ketone.*—A mixture of dibenzoylmethane (9·5 g.), 6-aminotetrahydrocarbazole (7·6 g.), and acetic acid (35 c.c.) was refluxed for 1 hour, and the solvent then removed by distillation under diminished pressure. The residue crystallised from alcohol in yellow prisms (8 g.), m. p. 229·5—230° (Found: C, 82·1; H, 6·2. $C_{27}H_{24}ON_2$ requires C, 82·6; H, 6·1%). This substance has very feebly basic properties, and when boiled with hydrochloric acid it first gives a red substance and is then slowly hydrolysed. Its solution in concentrated sulphuric acid is yellow and non-fluorescent, but on keeping the colour fades and a bright violet fluorescence develops; on the addition of water a red salt is precipitated.

2 : 4-*Diphenyl*-5 : 6-(4′ : 5′ : 6′ : 7′-*tetrahydroindolo*)(2′ : 3′)-*quinoline* (VII).—This substance may be obtained from the foregoing ketone in several ways, *e.g.*, (1) by keeping a cold sulphuric acid solution for 24 hours, (2) by heating a sulphuric acid solution to 60—65° for 5 minutes, (3) by passing hydrogen chloride into a solution in acetic acid, and (4) by heating it with half its weight of zinc chloride or phosphoric anhydride. The best procedure is the following: A mixture of the ketone (12·5 g.) and phosphoryl chloride (80 c.c.) was boiled for 1 hour, and the red liquid then gradually added to ice and water with stirring. The dull red solid was collected, washed with water, and triturated with ammonia; the resulting light yellow powder was collected, washed, dried at 105°, and extracted with ether in a Soxhlet apparatus from which air was excluded by means of carbon dioxide; the ethereal solution, on keeping, deposited yellow crystals which were collected and washed in an atmosphere of carbon dioxide, and finally dried in a vacuum desiccator (total yield, 9·5 g., 76%) (Found: C, 86·4; H, 6·1. $C_{27}H_{22}N_2$ requires C, 86·6; H, 5·9%). 2 : 4-*Diphenyl*-

5 : 6-(4′ : 5′ : 6′ : 7′-*tetrahydroindolo*)(2′ : 3′)-*quinoline* crystallises from ether in yellow prisms, m. p. 235°, and dissolves in most organic solvents to yellow solutions exhibiting a greenish-blue fluorescence. Its salts are red and sparingly soluble in water. The red solution in acetic acid gives a pink precipitate on addition of water, whilst the colourless solution in sulphuric acid exhibits a brilliant violet fluorescence. The *picrate*, prepared in alcoholic solution in an atmosphere of carbon dioxide, crystallised in orange-red needles, m. p. 241° (decomp. 243°). The most characteristic property of the base is the ease with which it absorbs oxygen from the air when in solution in organic solvents, especially ether or chloroform; it appears to be relatively stable in the solid state. The product, *dioxydiphenyltetrahydroindoloquinoline*, is readily isolated and crystallises from ether in long, colourless needles which decompose suddenly with bright incandescence at 168°, but without melting (Found: C, 79·4; H, 5·6; N, 6·7. $C_{27}H_{22}O_2N_2$ requires C, 79·8; H, 5·4; N, 6·9%). The dirty green solution in concentrated sulphuric acid slowly develops a most intense green fluorescence, giving the effect of opacity. The incandescence observed on heating suggests that this curious substance is a peroxide.

Metho-derivatives.—A mixture of the base (5 g.), pure methyl sulphate (3·6 g.), and benzene (140 c.c.) was boiled for 2·5 hours, air being displaced from the apparatus by nitrogen. The solvent was removed by distillation, the residual red oil dissolved in dry acetone (about 20 c.c.), and on keeping, red needles separated. These were collected (3·5 g.), and a further quantity (0·6 g.) could be obtained from the mother-liquor by concentration to two-thirds of its volume (further concentration gave uncrystallisable material). The separated *methosulphate* is sparingly soluble in acetone and moderately readily soluble in water. On heating, it decomposes at a high temperature without melting. The colourless solution in concentrated sulphuric acid exhibits a brilliant violet fluorescence. The related *methopicrate* crystallised from acetone in long, slender, meshed, orange-red needles, m. p. 252—254° (decomp.).

The methosulphate (4 g.) was added to benzene (100 c.c.) and 50% aqueous potassium hydroxide (50 c.c.), and the mixture heated for 1½ hours with occasional shaking; air in the apparatus was displaced by nitrogen. The bright red colour in both layers disappeared, the aqueous solution becoming colourless and the benzene layer intense brilliant green. In all the subsequent operations access of air was prevented by nitrogen. The aqueous layer was siphoned off and potassium hydroxide (35 g.) added to

the benzene layer, which was then boiled for 1 hour, filtered, and dried for 12 hours over potassium hydroxide. The solution was filtered, heated, and the base precipitated by the addition of boiling light petroleum (b. p. 60—80°) as a bright green solid, which was collected and dried in a vacuum. At this stage there was for the first time a momentary contact with air, but the desiccator had been previously filled with nitrogen and was quickly evacuated. Weighing was carried out with the utmost dispatch, since absorption of oxygen was obviously indicated during the operation (Found: C, 79·3, 78·8; H, 6·4, 6·3. $C_{28}H_{28}O_2N_2$ requires C, 79·2; H, 6·6%). The dark green powder becomes brown and then black when exposed to air. Treatment with acids gives red salts resembling the metho-salts mentioned above, and the solution in sulphuric acid exhibits violet fluorescence.

The authors desire to thank the Government Grant Committee of the Royal Society for a grant which defrayed a part of the cost of the work, and the Advisory Council of the Department of Scientific and Industrial Research for a grant that enabled one of them to take part in the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1927.]

CCCII.—*The Conversion of Palmatine into its Cryptopine Analogue (Cryptopalmatine).*

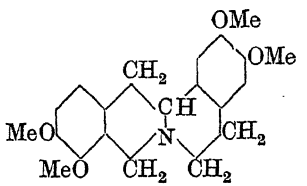
By ROBERT DOWNS HAWORTH, JOSEPH BLAKE KOEPFLI, and WILLIAM HENRY PERKIN, jun.

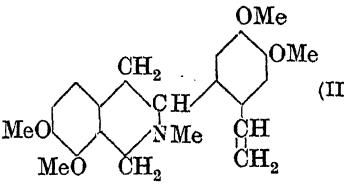
AN examination of the structural formulæ of the naturally occurring alkaloids of the ten-membered ring type, such as cryptopine and protopine, reveals the relationship between these alkaloids and those of the protoberberine series. Thus the protoberberine alkaloids berberine and coptisine (Kitasato, *Proc. Imp. Acad. Tokyo*, 1926, **2**, 124) are related to the ten-membered ring alkaloids β-homochelidonine and protopine, respectively. These relationships, together with the interconvertibility of the two types, leave little doubt that the further examination of natural products will result in the discovery of new affinities of the same kind. *epi*-Berberine, the protoberberine derivative corresponding to cryptopine, has so far not been isolated from natural sources, whilst the ten-membered ring analogue of palmatine has not been described either as a natural or as a synthetical product. This analogue of palmatine, for which we suggest the name "*cryptopalmatine*" (V), has now been obtained from palmatine by a process similar to that

employed in the synthesis of β-homochelidonine, cryptopine, and protopine (Haworth and Perkin, J., 1926, **129**, 445, 1769).

Tetrahydropalmatine (I) * was treated with methyl iodide and thus converted into the *methiodide* which exists in the usual α- and β-modifications, readily separable by crystallisation from methyl alcohol and then from water. The *β-methochloride*, obtained from the methiodide by the action of silver chloride, is a well-defined,

(I.)





(II.)

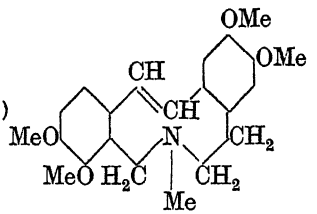
crystalline substance, whereas the corresponding *α-methochloride* has only been isolated as a hygroscopic syrup. When the methiodides or methochlorides are heated with methyl-alcoholic potassium hydroxide, *anhydromethyltetrahydropalmatine B* (II) is obtained as a crystalline substance, m. p. 115—116°, the constitution of which is proved by the facts (i) that it is a stable substance remaining unchanged after digestion with methyl alcohol or chloroform, and (ii) that its sparingly soluble, crystalline *hydrochloride* is not converted into tetrahydropalmatine methochloride by prolonged boiling with dilute hydrochloric acid.

Tetrahydropalmatine methiodide was next converted into the corresponding methohydroxide, by treatment with silver hydroxide in aqueous suspension, and the methohydroxide decomposed by evaporating the solution in a good vacuum, whereby a mixture of *anhydromethyltetrahydropalmatine A* (III) and B (II) was obtained, in which unfortunately the latter modification largely predominated. The former base possesses the properties characteristic of the "A" type, since it is unstable and is converted into tetrahydropalmatine methochloride by warming with dilute hydrochloric acid. Owing to the poor yield of this base, further experiments could only be carried out on a very small scale, and no attempt was made to isolate in a pure condition the amine oxide (IV), which results from the action of perbenzoic acid on the anhydro-base A (III). It was, however, observed that the amine oxide is soluble in water and yields a colourless, sparingly soluble *hydrochloride*. On warming with glacial acetic acid and hydrochloric acid, this amine oxide is readily converted into *cryptopalmatine* (V), a well-defined base which

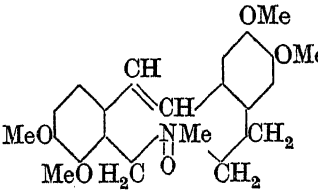
* We are indebted to Professor Späth for some of the palmatine iodide used in this investigation, but most of the material was prepared by us from berberine by the method of Späth and Quietensky (*Ber.*, 1925, **58**, 2267).

separates from ether in prisms, m. p. 148—150°, and, like cryptopine, gives a characteristic red-violet coloration with sulphuric acid.

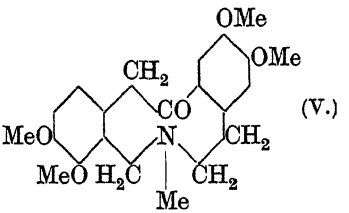
(III.)



(IV.)



(V.)



We hope, at a later date, to be able to obtain further quantities of cryptopalmatine, so that it may be possible to make a more complete examination of this interesting base.

Experimental.

Tetrahydropalmatine α- and β-Methiodides.—Tetrahydropalmatine (4 g.), methyl iodide (5 c.c.), and benzene (40 c.c.) were heated on the steam-bath for 4 hours, and the pale yellow methiodide (4·6 g.) was collected, dried, and fractionally crystallised from methyl alcohol (200 c.c.). The first fractions, recrystallised from water, yielded the *β-methiodide* as stout prisms, m. p. 266° (decomp.) * (Found: C, 53·0; H, 5·8. $C_{22}H_{28}O_4NI$ requires C, 53·1; H, 5·6%). This substance is very sparingly soluble in methyl alcohol or water. The last fractions from the crystallisation from methyl alcohol were recrystallised from water, and the *α-methiodide* separated in colourless prisms, m. p. 230°. The crystals contain water of crystallisation, but they lose it at 110° and fall to a powder (Found, in material dried at 110°: C, 53·2; H, 5·9).

Tetrahydropalmatine α- and β-Methochlorides.—The methiodide (*i.e.*, the mixture of the α- and β-forms), suspended in water, was heated with excess of silver chloride on the steam-bath for 3 hours. The filtered solution was concentrated to a small bulk, whereupon the *β-methochloride* separated and was collected. The mother-liquor, on further concentration, yielded the *α-methochloride* as a

* The melting points of the salts given in this and the following papers vary very much with the rate of heating, and must be considered as only approximate.

hygroscopic syrup. The β-methochloride crystallises from water in colourless prisms, m. p. 250° (decomp.) (Found: C, 64·8; H, 7·2. $C_{22}H_{28}O_4NCl$ requires C, 65·1; H, 6·9%). The α-methochloride separates from water as a syrup, which is readily soluble in alcohol and is precipitated as an oil on the addition of ether. It is converted into the α-methiodide, m. p. 230°, by the addition of potassium iodide to the aqueous solution.

Anhydromethyltetrahydropalmatine B (II).—Tetrahydropalmatine methochloride was heated on the steam-bath for 2 hours with excess of 10% methyl-alcoholic potassium hydroxide. The solution was diluted with water, the oily base extracted with ether, and the extract dried, filtered, and concentrated; *anhydromethyltetrahydropalmatine B* then separated in stout, colourless prisms, m. p. 115—116° (Found: C, 71·3; H, 7·5. $C_{22}H_{27}O_4N$ requires C, 71·5; H, 7·3%). This base is very soluble in the usual organic solvents with the exception of petroleum. It is stable towards hot aqueous methyl alcohol or chloroform and yields a sparingly soluble *hydrochloride* which crystallises from water in nodular clusters of needles, m. p. 210° (decomp.); these contain water of crystallisation some of which is lost at 100°, the crystals falling to a powder, but 1 mol. of water is retained after drying at 110° (Found, in material dried at 110°: C, 63·0; H, 7·1. $C_{22}H_{28}O_4NCl,H_2O$ requires C, 62·4; H, 7·1%).

Anhydromethyltetrahydropalmatine A (III).—Tetrahydropalmatine methiodide (3 g.) was digested with a suspension of silver hydroxide until conversion into the methohydroxide was complete. The filtered solution was evaporated and the residue heated for an hour at 100°, both processes being conducted in a vacuum. The syrup which remained was extracted several times with ether, in order to separate the anhydro-bases from any undecomposed methohydroxide, and the ether allowed to evaporate slowly; *anhydromethyltetrahydropalmatine A* gradually separated in needles (0·1 g.), m. p. 131—132° (Found: C, 71·5; H, 7·1. $C_{22}H_{27}O_4N$ requires C, 71·5; H, 7·3%), whilst the modification B (1·5 g.) slowly crystallised from the mother-liquors. Anhydromethyltetrahydropalmatine A is an unstable base which dissolves in cold dilute hydrochloric acid and may be liberated from the solution by sodium hydroxide. After boiling in dilute acid for some time, the base does not separate on the addition of sodium hydroxide, conversion into tetrahydropalmatine methochloride evidently having taken place.

Cryptopalmatine (V).—Anhydromethyltetrahydropalmatine A (0·2 g.) in chloroform (5 c.c.) was gradually added to an ice-cold ethereal solution of perbenzoic acid (0·25 g. in 25 c.c.). The mixture was kept over-night during which it acquired a greenish-yellow tint,

but no crystalline material separated as in the cases previously examined (Haworth and Perkin, *loc. cit.*). When the mixture was shaken with very dilute hydrochloric acid and the extract concentrated in a vacuum, the *hydrochloride* of the amine oxide (IV) separated in colourless prisms, m. p. 198—200° (decomp.) with previous darkening. Owing to scarcity of material the amine oxide was not isolated, but it was observed to be soluble in water because an aqueous solution of the hydrochloride remained clear on the addition of sodium hydroxide.

The hydrochloride (0·1 g.) was dissolved in glacial acetic acid (2 c.c.) and concentrated hydrochloric acid (2 c.c.), boiled for 2 minutes, the brown solution diluted with water, made alkaline with sodium hydroxide, and the amorphous base extracted with chloroform; when the extract was dried and the solvent removed, a brown semi-solid mass remained. This was dissolved in a little alcohol, mixed with a large volume of ether, filtered from amorphous material, the ethereal solution well washed with water, dried over potassium carbonate, filtered, and the solvent allowed to evaporate slowly, whereupon *cryptopalmatine* separated in small, colourless prisms, m. p. 148—150° (Found: C, 68·6; H, 6·8. $C_{22}H_{27}O_5N$ requires C, 68·8; H, 7·0%). A solution of the base in glacial acetic acid developed a reddish-violet coloration on the addition of concentrated sulphuric acid.

THE DYSON PERRINS LABORATORY,
OXFORD.
ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE.

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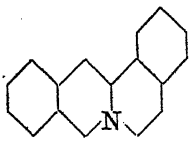
CCCIII.—*Synthetical Experiments in the* iso*Quinoline Group. Part VII. A Synthesis of* 3:11-*Dimethoxyprotoberberinium Salts.*

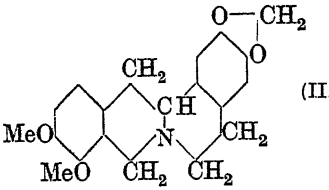
By SATYENDRA NATH CHAKRAVARTI, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

A COMPARISON of the constitutional formulæ of groups of alkaloids brings to light many curious generalities. It is difficult to understand why so many of these substances are built up on a common skeleton and why certain groups, and more particularly methoxy- and methylenedioxy-groups, should play so prominent a part in their structure. Attention has already been directed to the fact (J., 1926, 33) that the alkaloids palmatine, berberine, corydaline, and many others are all derived from the same angular structure (I),

a point clearly illustrated by the formula of tetrahydroberberine (II). It was also pointed out that β-homochelidonine, cryptopine,

(I.)

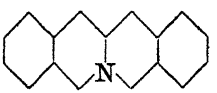


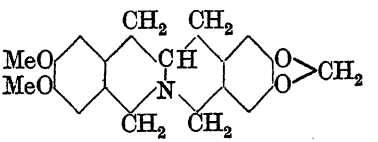


(II.)

and protopine, although not actually derivatives of (I), readily yield quaternary salts which are built up on this skeleton. In order to obtain some light on the reason why the skeleton (I) is so commonly selected by nature, the alkaloid 2 : 3-methylenedioxy-11 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine (IV),* isomeric with tetrahydroberberine, but differing from it in containing the linear structure (III), was synthesised (*loc. cit.*, p. 42).

(III.)





(IV.)

During the course of those experiments, it soon became evident that the various stages in the synthesis did not proceed so smoothly as in the case of the corresponding stages in the synthesis of tetrahydro-ψ-berberine, and furthermore, the properties of the substance (IV) were not nearly so definite and characteristic as those of tetrahydroberberine. In particular, the property of yielding highly coloured quaternary salts on treatment with iodine or other oxidising agents, so strikingly shown by tetrahydroberberine, fails entirely in the case of the paraberine analogue (*loc. cit.*, p. 37). These observations led to the suggestion that the greater ease of formation and more characteristic properties of alkaloids built up on the angular type may have some bearing on the occurrence and preferential selection of this type in nature.

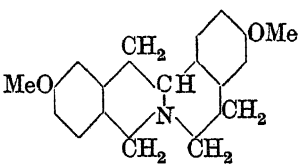
Another remarkable feature, not only of the alkaloids of the berberine group, but also of many others of widely different origin, *e.g.*, narcotine, cryptopine, corycavidine, and glaucine, is the occurrence in the molecule of two catechol nuclei, usually modified by methoxy- or methylenedioxy-groups, although in some cases, *e.g.*, corydine and corytuberine, a hydroxy-group remains free. There can be no doubt that the presence of these methoxy- and methylenedioxy-groups has a profound bearing on the ease of synthesis and

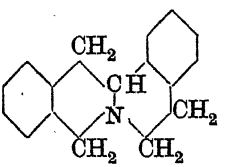
* This alkaloid is actually more directly related to tetrahydro-ψ-*epi*berberine (J., 1924, 125, 1677).

characteristic properties of these alkaloids, and there are also indications, to which reference has been made (this vol., p. 2262), that these groups also greatly influence the possibility of converting the alkaloids into derivatives of the ten-membered ring type (compare J., 1926, 446), and consequently into alkaloids of the β-homochelidonine group. In view of these considerations it seemed to be of interest to attempt to prepare alkaloids which, although built up on the angular skeleton (I), do not contain a catechol nucleus, and to compare the ease of synthesis and characteristic properties of such substances with these features in the case of the alkaloids of the palmatine–berberine type.

The present communication deals with the synthesis of 3 : 11-*dimethoxytetrahydroprotoberberine* (V) * containing two methoxy-groups, and in the succeeding investigation we describe the synthesis of tetrahydroprotoberberine itself (VI), which contains no methoxy-groups and to which special interest attaches because it is the parent of the whole palmatine–berberine group of alkaloids.

(V.)





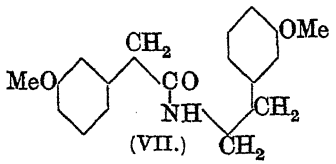
(VI.)

The synthesis of 3 : 11-dimethoxyprotoberberine and its derivatives was conducted in the following manner. β-*m*-Methoxyphenylethylamine, prepared by a slight modification of the method of Helfer (*Helv. Chim. Acta*, 1924, **7**, 945), was condensed with *m*-methoxyphenylacetic acid, prepared by a method similar to that employed by Pschorr (*Annalen*, 1912, **391**, 41), and the m-*methoxyphenylaceto*-β-m-*methoxyphenylethylamide* (VII) so obtained was converted, in a yield of 80%, into a syrupy base of which the *picrate* is crystalline. This base, which is probably 6-*methoxy*-1-(3′-*methoxybenzyl*)-3 : 4-*dihydro*isoquinoline (VIII), oxidises rapidly on exposure to air and is readily reduced by zinc and sulphuric acid to 6-*methoxy*-1-(3′-*methoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (IX), an oily base yielding a crystalline *sulphate* and *picrate*. Ring-closure of the *formyl* derivative was effected in the usual manner with phosphorus oxychloride, giving a 66% yield of a yellow crystalline base, m. p. 130°, which is doubtless 3 : 11-*dimethoxydihydroprotoberberine* (X).

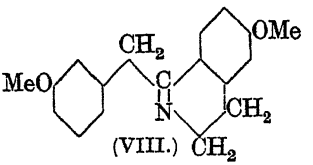
Although we have no direct evidence that the two ring-closures, *i.e.*, the conversion of (VII) into (VIII) and (IX) into (X), have taken place in the para-positions to the methoxy-groups, there can be little doubt that this is the case, since, judging from analogy,

* The nomenclature is discussed in J., 1925, **127**, 1462.

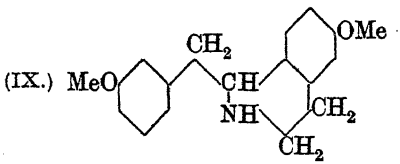
ring-closure in the ortho-positions is most unlikely. Synthetical experiments which are in progress will, we hope, decide this point.

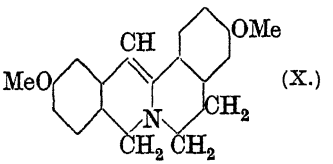


(VII.)

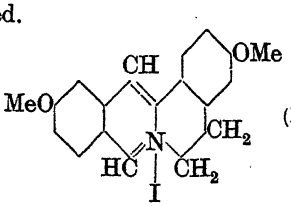


(VIII.)



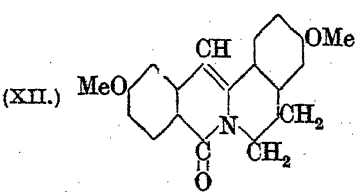


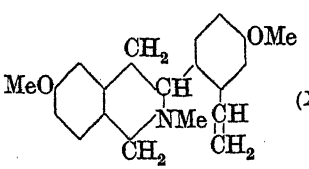
Dimethoxydihydroprotoberberine (X) gives well-characterised, pale yellow salts of which the *hydrochloride*, the *hydriodide*, and the *picrate* are described. It is reduced by zinc dust and sulphuric acid to 3 : 11-dimethoxytetrahydroprotoberberine (V), a colourless crystalline base, m. p. 111°, which may also be obtained, although in smaller yield, from (IX) by condensation with formaldehyde. Of the colourless crystalline salts, the *hydrochloride*, *hydriodide*, and *picrate* are described.



(XI.)

When 3 : 11-dimethoxytetrahydroprotoberberine (V) is oxidised with iodine in alcoholic solution, it yields 3 : 11-*dimethoxyprotoberberinium iodide* (XI), a yellow quaternary salt from which the corresponding yellow *chloride* was prepared. The iodide (XI) is decomposed in the usual manner by potassium hydroxide giving 3 : 11-*dimethoxyoxyprotoberberine* (XII) and dimethoxydihydroprotoberberine (X), which are readily separated, in that the former is insoluble and the latter soluble in dilute mineral acids.





(XIII.)

3 : 11-*Dimethoxytetrahydroprotoberberine methiodide*, obtained by heating the base (V) with methyl iodide, was readily separated into

α- and β-forms by crystallisation from water (compare Pyman, J., 1913, **103**, 825; Haworth and Perkin, J., 1926, 1772), and these were converted into the corresponding *methochlorides*, of which the β-form is crystalline, whereas the α-modification is a syrup. The methiodide was next converted into *anhydromethyl*-3 : 11-*dimethoxytetrahydroprotoberberine B* (XIII) by the action of alcoholic potassium hydroxide, and the interesting observation was made that this is the only base which is obtained when the methiodide is converted by silver hydroxide into the corresponding methohydroxide and the aqueous solution is evaporated in a good vacuum. The structure assigned to this base is confirmed by its stability towards aqueous methyl alcohol and chloroform, and by its yielding a stable and sparingly soluble *hydrochloride*. It is clear from these experiments that the presence of two methoxy-groups attached to the annular skeleton of tetrahydroberberine as in (V) does not allow the formation of the ten-membered ring, at all events under the usual conditions.

The other points of general interest which emerge from this investigation are (i) that the synthetical experiments described proceed almost as readily, if perhaps not quite so smoothly, when only two methoxy-groups are present as they do in the case of the corresponding syntheses in the berberine series, and (ii) that the deep yellow colour of the salts of berberine and allied alkaloids becomes much less intense when only two methoxy-groups are present in the molecule.

EXPERIMENTAL.

m-Methoxybenzaldehyde is obtained in a yield of 80% by the following method : *m*-Hydroxybenzaldehyde (250 g.), methyl alcohol (750 c.c.), and sodium hydroxide (85 g.), dissolved in the minimum of water, are heated on the steam-bath, and freshly distilled methyl sulphate (290 g.) is added sufficiently rapidly to maintain brisk ebullition; a further quantity of methyl sulphate (200 g.) is then added, the mixture being kept alkaline by the addition of 50% sodium hydroxide. The product is kept for ½ hour, the methyl alcohol removed by distillation, and the residue diluted with water and extracted with ether. The extract is dried with sodium sulphate, the ether removed, and the *m*-methoxybenzaldehyde distilled under reduced pressure. *m*-Methoxycinnamic acid was prepared by heating *m*-methoxybenzaldehyde (100 g.), malonic acid (160 g.), and piperidine (5 c.c.) in pyridine (250 c.c.) solution for 1½ hours on the steam-bath, and then boiling for 15 minutes on the sand-bath. The product, on being poured into excess of dilute hydrochloric acid, gave an almost quantitative yield of *m*-methoxycinnamic acid, m. p. 117°. This acid was reduced with sodium amalgam to β-*m*-methoxyphenylpropionic acid in the manner described by Helfer (*loc. cit.*).

m-Methoxyphenylacetic acid was prepared by the method of Pschorr (*loc. cit.*), but a different procedure was adopted in the separation of the products of the hydrolysis of the az-lactone. After hydrolysing the latter with sodium hydroxide, the solution was saturated with sulphur dioxide, the benzoic acid collected, the filtrate acidified and boiled, and the m-*methoxyphenylpyruvic acid* collected and recrystallised from glacial acetic acid, separating in small crystals, m. p. 150° (Found: C, 61·6; H, 5·1. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·1%). This acid is readily soluble in hot alcohol but rather sparingly soluble in cold acetic acid or toluene. It was oxidised in cold alkaline solution with hydrogen peroxide, and *m*-methoxyphenylacetic acid, m. p. 68°, was obtained in good yield on acidifying the alkaline solution.

m-*Methoxyphenylacet*-β-m-*methoxyphenylethylamide* (VII).—(i) Equivalent quantities of β-*m*-methoxyphenylethylamine (Helfer, *loc. cit.*) and *m*-methoxyphenylacetic acid were heated at 180° for 3 hours. Alternatively, (ii) *m*-methoxyphenylacetic acid (6 g.), dissolved in a little chloroform, was gently boiled for ½ hour with thionyl chloride (3·5 g.); the chloroform was removed and the residual yellow oil added to an emulsion of β-*m*-methoxyphenylethylamine (5 g.) in potassium hydroxide (40 c.c. of 10%), the mixture being well shaken during the addition. By either method, the *amide* was obtained as an oil which did not crystallise in contact with the usual solvents.

6-*Methoxy*-1-(3′-*methoxybenzyl*)-3 : 4-*dihydro*isoquinoline (VIII).—The amide just described (20 g.) was heated with phosphorus oxychloride (50 c.c.) for 2 hours on the steam-bath and then kept over-night. The mixture was decomposed and extracted with hot water (charcoal), filtered from tar, the filtrate made alkaline with sodium hydroxide, and extracted several times with benzene (A). Some of the benzene extract was dried over potassium carbonate, the solvent removed, and the oily base dissolved in alcohol and mixed with an alcoholic solution of picric acid. The yellow *picrate* of (VIII) which separated is sparingly soluble in alcohol and readily soluble in hot glacial acetic acid, from which it separates in small needles, m. p. 155° (Found: C, 56·3; H, 4·6. $C_{24}H_{22}O_9N_4$ requires C, 56·5; H, 4·3%).

6-*Methoxy*-1-(3′-*methoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (IX).—This was obtained by extracting the benzene extract (A) with dilute sulphuric acid, and reducing the acid solution with zinc dust. The solution was made alkaline with ammonia, the tetrahydro-base extracted with chloroform, dried over potassium carbonate, and the solvent removed, leaving the base as an oil. The *hydrochloride*, obtained by dissolving the oil in hot dilute hydro-

chloric acid, and cooling, separated in needles, m. p. 192° (decomp.) (Found: C, 67·9; H, 6·9. $C_{18}H_{22}O_2NCl$ requires C, 67·6; H, 6·9%). The *sulphate* is readily soluble in hot water and crystallises in rhombs. The *picrate*, prepared in alcoholic solution, is sparingly soluble in hot alcohol, and separates from glacial acetic acid as a crystalline powder, m. p. 148° (Found: C, 56·6; H, 4·6. $C_{24}H_{24}O_9N_4$ requires C, 56·3; H, 4·8%).

3 : 11-*Dimethoxydihydroprotoberberine* (X).—The N-*formyl* derivative of (IX) was prepared by adding a slight excess of formic acid to a dry benzene solution of the base; the benzene was removed, and the residue heated in an oil-bath at 200° for 2 hours. The whole (13 g.) was dissolved in dry toluene (50 c.c.), phosphorus oxychloride (30 c.c.) added, and the mixture boiled for 1½ hours. The product was diluted with petroleum ether, the dark brown oil which separated was dissolved in alcohol, made alkaline with sodium hydroxide, and diluted with water; when the sides of the vessel were scratched vigorously, the *base* (X) separated as a yellow powder (8 g.), which crystallised from alcohol or benzene in shining, yellow, rhombic prisms, m. p. 130° (Found: C, 78·0; H, 6·6. $C_{19}H_{19}O_2N$ requires C, 77·8; H, 6·5%). This base is sparingly soluble in alcohol, more soluble in benzene, and readily soluble in chloroform. It is a strong base yielding pale yellow, crystalline salts with mineral acids. The solution in concentrated sulphuric acid is yellowish-brown and becomes deep red on the addition of a crystal of potassium nitrate. The *hydrochloride* is rather sparingly soluble in water or dilute hydrochloric acid, and crystallises from the former in silky needles containing $4H_2O$ which is lost at 105° (Found: loss at 105°, 17·0. Calc. for $4H_2O$: 17·9. Found in material dried at 105°: C, 68·7; H, 6·1. $C_{19}H_{20}O_2NCl$ requires C, 69·2; H, 6·1%). The *hydriodide*, obtained by adding sodium iodide to the aqueous solution of the hydrochloride, is a yellow, crystalline powder, very sparingly soluble in boiling water (Found: C, 54·6; H, 4·8. $C_{19}H_{20}O_2NI$ requires C, 54·2; H, 4·8%). The *picrate*, prepared in alcoholic solution, is very sparingly soluble in alcohol, and separates from glacial acetic acid as a bright yellow, crystalline powder, m. p. 232° (Found: C, 57·4; H, 4·1. $C_{25}H_{22}O_9N_4$ requires C, 57·5; H, 4·2%).

3 : 11-*Dimethoxytetrahydroprotoberberine* (V).—This substance was obtained in two ways. (i) Dimethoxydihydroprotoberberine (X) was reduced by zinc dust and dilute sulphuric acid until the solution became colourless; the product was filtered, the filtrate made alkaline with ammonia, the base extracted with chloroform, dried over potassium carbonate, the solvent removed, and the residue dissolved in dilute hydrochloric acid, from which the *hydrochloride* of the base separated on cooling. This was collected, dissolved in

water, decomposed with concentrated ammonia, and the almost colourless 3 : 11-*dimethoxytetrahydroprotoberberine* crystallised from alcohol or dry benzene. (ii) The tetrahydro-base (IX; p. 2270) was dissolved in methyl alcohol, mixed with sodium bicarbonate and a slight excess of 40% formaldehyde, and the mixture warmed for a few minutes on the steam-bath; on the addition of water and some salt, a gum separated, which was thoroughly washed with cold water and heated with concentrated hydrochloric acid on the steam-bath for a few minutes; the gummy hydrochloride was redissolved in water, decomposed with ammonia, the base extracted with chloroform, and the solvent removed. The residual syrup was rubbed with ether, which removed unchanged tetrahydro-base, and the sparingly soluble residue of dimethoxytetrahydroprotoberberine was crystallised from alcohol or benzene. The yield was small, however, and various modifications of this method failed to effect much improvement.

3 : 11-Dimethoxytetrahydroprotoberberine separates from alcohol or dry benzene in jagged prisms, m. p. 111° (Found: C, 77·6; H, 7·1. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·1%), readily soluble in chloroform, or in methyl or ethyl alcohol; the base and its salts are rather more soluble than dimethoxydihydroprotoberberine and its salts. The hydrochloride is readily soluble in hot water, from which it separates in characteristic, colourless rosettes, m. p. 199° (Found: C, 68·8; H, 6·7. $C_{19}H_{22}O_2NCl$ requires C, 68·8; H, 6·6%). The *hydriodide*, obtained by adding sodium iodide to the aqueous solution of the hydrochloride, is moderately soluble in boiling water and separates as a crystalline powder with a very slight yellow tinge, m. p. 205° (Found: C, 54·4; H, 5·2. $C_{19}H_{22}O_2NI$ requires C, 53·9; H, 5·2%). The *picrate*, prepared in alcoholic solution, separates from glacial acetic acid or alcohol in bright yellow needles, m. p. 139—140° (decomp.) (Found: C, 57·5; H, 4·9. $C_{25}H_{24}O_9N_4$ requires C, 57·3; H, 4·6%).

The 3 : 11-*Dimethoxyprotoberberinium Salts*.—Dimethoxytetrahydroprotoberberine (V), dissolved in the minimum of boiling alcohol, was mixed with anhydrous sodium acetate, and an alcoholic solution of iodine slowly added until a permanent coloration remained. The dark brown granular *periodide* was collected, washed with water, suspended in hot water, and decomposed by adding aqueous sulphurous acid. The pale yellow *iodide* (XI) separated from water, in which it is very sparingly soluble, in pale yellow needles, m. p. 242° (Found: C, 54·2; H, 4·4. $C_{19}H_{18}O_2NI$ requires C, 54·4; H, 4·3%). The *chloride* is readily obtained by digesting an aqueous suspension of the iodide with excess of silver chloride for 2 hours on the steam-bath; after filtering, concentrating, and adding hydrochloric acid,

the mass of pale yellow needles of the chloride is recrystallised from dilute hydrochloric acid and left on porous porcelain exposed to air for 2 days, m. p. 200° (decomp.). The salt contains $3H_2O$ which is lost at 105° (Found: loss at 105°, 13·5. Calc. for $3H_2O$: 14·1. Found in material dried at 105°: C, 69·3; H, 5·8. $C_{19}H_{18}O_2NCl$ requires C, 69·6; H, 5·5%). The *picrate* was obtained, by adding aqueous picric acid to the hot aqueous solution of the chloride, as yellow flocks almost insoluble in alcohol and sparingly soluble in glacial acetic acid, from which it separates as a feathery mass of long, yellow needles, m. p. 238° (Found: C, 55·5; H, 3·9. $C_{25}H_{22}O_{10}N_4$ requires C, 55·8; H, 4·1%).

3 : 11-*Dimethoxyoxyprotoberberine* (XII).—A boiling aqueous solution of 3 : 11-dimethoxyprotoberberinium chloride (2 g.) was added to a hot solution of potassium hydroxide (8 g.) in water (32 c.c.), and the whole heated on the steam-bath for 2 hours. The yellow mass which separated was collected and thoroughly extracted with dilute hydrochloric acid (A); the residue was dissolved in hot glacial acetic acid, mixed with an equal volume of boiling water, and allowed to stand, the oxy-derivative (XII) then separating as a mass of colourless needles, m. p. 143° (Found: C, 74·1; H, 5·7. $C_{19}H_{17}O_3N$ requires C, 74·3; H, 5·5%). 3 : 11-*Dimethoxyoxyprotoberberine* is sparingly soluble in the usual solvents, except glacial acetic acid, and insoluble in dilute mineral acids. It dissolves in concentrated sulphuric acid to a yellow solution which changes to brown on the addition of a crystal of potassium nitrate.

The hydrochloric acid extracts (A) gradually deposited a mass of pale yellow needles, which were collected, dissolved in water, and precipitated with ammonia. The precipitate was washed and recrystallised from alcohol; the resulting yellow rhombic prisms, m. p. 130°, proved to be identical with the 3 : 11-dimethoxydihydroprotoberberine (X) described on p. 2271.

3 : 11-*Dimethoxytetrahydroprotoberberine Methiodide*.—The base (V; 10 g.) and methyl iodide (15 c.c.) were boiled for 15 minutes, the excess of methyl iodide was removed, and the residue dissolved in boiling water (300 c.c.) and cooled; the β-*methiodide* separated and was crystallised from water as colourless prisms, m. p. 245° (decomp.) (Found: C, 54·9; H, 5·7. $C_{20}H_{24}O_2NI$ requires C, 54·9; H, 5·5%). The α-*methiodide*, obtained by concentrating the mother-liquors, separated from water in colourless nodules, m. p. 224° (Found: C, 55·2; H, 5·6). The methochlorides were obtained by digesting an aqueous suspension of the mixed methiodides with silver chloride. The filtered solution was evaporated to dryness, the pale yellow syrup dissolved in alcohol, and ether slowly added; the β-*methochloride* then separated in colourless needles, m. p. 245° (decomp.).

(Found: C, 69·2; H, 7·1. $C_{20}H_{24}O_2NCl$ requires C, 69·4; H, 6·9%). The *α-methochloride* was precipitated as a syrup by the addition of more ether to the alcohol–ether mother-liquor of the β-methochloride. It was not obtained in a crystalline state, but the addition of sodium iodide to its aqueous solution precipitated the α-methiodide, m. p. 224°.

Anhydromethyl-3 : 11-*dimethoxytetrahydroprotoberberine* (XIII).—(i) The mixed methochlorides (1 g.) were boiled with 25% methyl-alcoholic potassium hydroxide (6 c.c.) for 2 hours, the mixture was diluted with water, the oily base extracted with ether, and the solvent removed, leaving the crude base as a colourless oil which did not solidify; it was soluble in the usual organic solvents and yielded the sparingly soluble *hydrochloride* (see below) when it was stirred with dilute hydrochloric acid. (ii) An aqueous solution of the mixed methiodides or methochlorides was decomposed with silver hydroxide, filtered, the filtrate concentrated in a good vacuum, and the residue extracted with benzene. This left a small amount of material which was dissolved in water and concentrated, giving crystals of 3 : 11-*dimethoxytetrahydroprotoberberine methocarbonate*, m. p. 216°, which dissolved with effervescence in dilute hydrochloric acid (Found: C, 67·9; H, 6·9. $C_{21}H_{25}O_5N$ requires C, 67·9; H, 6·7%). The benzene extract, on concentration, yielded an oil which gave a sparingly soluble hydrochloride and was identical with the oil obtained by method (i); all its properties showed that it was an anhydro-base of the "B" type. *Anhydro*-3 : 11-*dimethoxytetrahydroprotoberberine B* is an oil which decolorises a solution of bromine in chloroform and also an acid solution of permanganate. It is recovered after boiling for several hours with aqueous alcohol or chloroform. The sparingly soluble hydrochloride crystallises from water in small needles, m. p. 236° (decomp.), and is recovered unchanged after boiling with dilute hydrochloric acid for 6 hours (Found: C, 69·2; H, 6·9. $C_{20}H_{24}O_2NCl$ requires C, 69·4; H, 6·9%). When the base (XIII) was mixed with perbenzoic acid, no crystalline material separated. The mixture was extracted with dilute hydrochloric acid, the acid extract evaporated in a vacuum, and the resulting gum warmed with glacial acetic acid and concentrated hydrochloric acid. The reddish solution obtained yielded an amorphous, dark slime on the addition of ammonia, but no crystalline substance could be isolated from it.

THE DYSON PERRINS LABORATORY,
OXFORD.
[*Received, August 5th*, 1927.]
THE ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE.

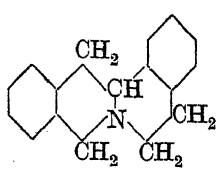
CCCIV.—*Synthetical Experiments in the* iso*Quinoline Group. Part VIII. A Synthesis of Protoberberinium Salts.*

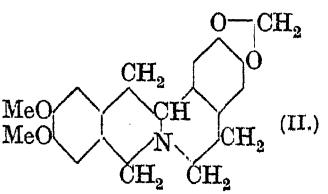
By SATYENDRA NATH CHAKRAVARTI, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

IT is pointed out (preceding paper) that the parent substance of the alkaloids of the palmatine–berberine series is protoberberine, the synthesis of which is now described. It was thought probable that the methods which had proved so successful in the syntheses of ψ-berberine and other similar cases might fail in the present case because the absence of the methylenedioxy- or methoxy-groups might inhibit one or other of the necessary ring-closures. These anticipations were, in fact, largely realised, for although the synthesis was ultimately successful, the yields obtained, especially in the case of the second ring-closure, were so poor that the accumulation of sufficient material for the study of protoberberine was a very tedious process. Clearly, then, the presence of the catechol nuclei is an important factor in facilitating the building up of these alkaloids, and this fact is in harmony with the presence of these nuclei in so many of the naturally occurring alkaloids of this and similar groups.

As in previous cases, the first object was the synthesis of *tetrahydroprotoberberine* (I), and the methods employed were similar to those which had been successful in the synthesis of tetrahydro-ψ-berberine (II) and allied substances. Phenylacet-β-phenylethylamide, prepared from phenylacetic acid and β-phenylethylamine,

(I.)

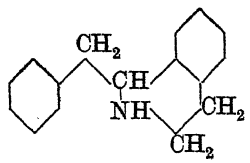


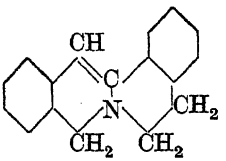


(II.)

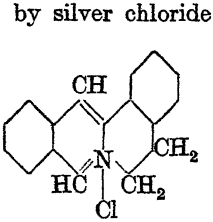
was converted into 1-benzyl-3 : 4-dihydro*iso*quinoline by the action of phosphorus pentoxide (compare Decker and Kropp, *Ber.*, 1909, **42**, 2075; Pictet and Kay, *ibid.*, p. 1976; Forsyth, Kelly, and Pyman, J., 1925, **127**, 1663). On reduction with dilute sulphuric acid and zinc, the dihydro-base yielded 1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III; compare Forsyth, Kelly, and Pyman, *loc. cit.*, p. 1664), an oily base which gives a crystalline hydriodide and *sulphate*. The conversion of this substance into tetrahydroprotoberberine (I) presented considerable difficulty. The usual con-

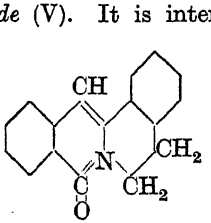
densation with formaldehyde was unsuccessful, but it was ultimately found that treatment of the N-*formyl* derivative with phosphorus

(III.) 

 (IV.)

oxychloride under strictly defined conditions (see p. 2278) yielded small quantities of *dihydroprotoberberine* (IV), the yield under the most favourable conditions not exceeding 10%. (The substitution of phosphorus pentoxide for the oxychloride did not effect any improvement.) The base (IV) was not isolated as such, but was immediately reduced by zinc dust and hydrochloric acid to tetrahydroprotoberberine (I), m. p. 85°, which crystallises well and yields a crystalline *hydrochloride* and *picrate*. When the tetrahydro-base is oxidised in alcoholic solution by iodine, it is converted into *protoberberinium iodide*, which is much less highly coloured than berberinium iodide, crystallises in yellow needles, and is converted by silver chloride into the *chloride* (V). It is interesting

(V.) 

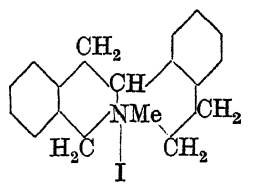
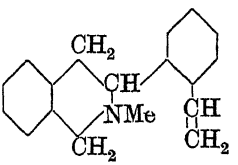
 (VI.)

that this salt crystallises from water with $4H_2O$, thus resembling berberinium chloride and the other analogously constituted chlorides of this series, all of which contain water of crystallisation. In this case, again, the loss of colour is very striking, since the intense yellow so characteristic of berberinium chloride has almost disappeared in the case of protoberberinium chloride, the crystals of which have only a pale yellow tinge.

Protoberberinium chloride is decomposed by potassium hydroxide in the usual manner and yields *oxyprotoberberine* (VI), m. p. 102°, but the dihydroprotoberberine which is evidently produced at the same time could not be isolated in a pure state owing to the small amount of material at our disposal. Attention may be directed to the unexpectedly large effect which the elimination of methoxy- and methylenedioxy-groups has in producing low melting points in the derivatives of protoberberine: thus tetrahydroprotoberberine has m. p. 85°, whereas tetrahydroberberine melts at 170° and

tetrahydropalmatine at 147°; oxyprotoberberine has m. p. 102°, whereas oxyberberine melts at 200° and oxypalmatine at 183°.

Tetrahydroprotoberberine methiodide (VII), prepared by heating the base with excess of methyl iodide, was readily separable into α- and β-forms. When treated with alcoholic potassium hydroxide, the methiodide was converted into *anhydromethyltetrahydroprotoberberine* (VIII), a syrupy base which yields a sparingly soluble *hydrochloride*. The same anhydro-base was obtained when the

(VII.)  (VIII.) 

methiodide was digested with silver hydroxide and the solution evaporated in a good vacuum. No trace of the isomeric base containing a ten-membered ring could be isolated, and the constitution (VIII) is assigned to anhydromethyltetrahydroprotoberberine because the base is stable towards methyl alcohol and chloroform, and the sparingly soluble hydrochloride is also stable towards boiling dilute hydrochloric acid—conditions under which the ten-membered isomeride would be converted into a quaternary chloride. It would appear, therefore, that, in the absence of methoxy- or methylenedioxy-groups, there is no tendency towards the formation of the ten-membered anhydro-base.

EXPERIMENTAL.

1-*Benzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (III).—To a boiling solution in xylene (100 c.c.) of phenylacet-β-phenylethylamide (20 g.), obtained by heating molecular proportions of phenylacetic acid and β-phenylethylamine at 180° (Decker and Kropp, *loc. cit.*), phosphorus pentoxide (40 g.) was added, and the boiling continued for ¼ hour; the mixture was poured into water, the toluene layer removed, and the aqueous layer made strongly alkaline with sodium hydroxide. The 1-benzyl-3 : 4-dihydro*iso*quinoline which separated as an oil (Pictet and Kay, *loc. cit.*) was rapidly extracted with benzene and thence with dilute sulphuric acid; the acid extract gradually deposited the *sulphate* in regular cubes, m. p. 216° (Found : C, 60·4; H, 5·4. $C_{16}H_{15}N,H_2SO_4$ requires C, 60·2; H, 5·3%). The sulphuric acid solution of the sulphate was heated with excess of zinc dust for 1½ hours, reduction then being complete. The hot solution was filtered, decomposed with ammonia, the oily base

extracted with chloroform, the extract dried over potassium carbonate, the solvent removed, and the residual oil dissolved in hot dilute sulphuric acid. The *1-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline sulphate*, which gradually formed, crystallised from water with $5H_2O$, of which $4H_2O$ were lost at 100°, m. p. 191° (decomp.) [Found: loss at 100°, 11·2. $(C_{16}H_{17}N)_2,H_2SO_4,5H_2O$ requires $4H_2O$, 11·2. Found in material dried at 100°: C, 67·8; H, 6·7. $(C_{16}H_{17}N)_2,H_2SO_4,H_2O$ requires C, 68·3; H, 6·8%]. This sulphate is less soluble in dilute sulphuric acid than in water.

Tetrahydroprotoberberine (I).—This base could not be obtained by treating the foregoing base with formaldehyde in the usual manner. A variety of conditions were examined and, although small quantities of crystalline hydrochlorides were sometimes formed, they always gave rise to gummy bases on decomposition with alkali. Ultimately the following method was found to give the desired result although the yield was not more than 10%. 1-Benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (24 g.) and anhydrous formic acid (5 g.) were heated in an oil bath at 200—205° until effervescence had ceased (3 hours). The product was dissolved in toluene and boiled with phosphorus oxychloride (48 c.c.) for 1½ hours; light petroleum was then added, the clear liquid decanted from the dark-coloured gum, the latter extracted with dilute hydrochloric acid (charcoal), and the solution of dihydroprotoberberine hydrochloride reduced by heating with excess of zinc dust for 2 hours, during which the yellow solution became colourless. The hot liquid was filtered, the filtrate decomposed with ammonia, the base extracted with chloroform, dried over potassium carbonate, the chloroform removed, and the residue dissolved in hot dilute hydrochloric acid, from which *tetrahydroprotoberberine hydrochloride* gradually separated. This was collected, recrystallised from water (charcoal), the purified salt dissolved in water, decomposed with ammonia, the base extracted with ether, dried over potassium carbonate, filtered, and the ether allowed to evaporate slowly, whereupon *tetrahydroprotoberberine* crystallised in clusters of colourless needles, m. p. 85° (Found: C, 87·2; H, 7·3. $C_{17}H_{17}N$ requires C, 86·8; H, 7·2%); it dissolves readily in the usual organic solvents, with the exception of petroleum, and crystallises well from either ether or methyl alcohol. It is a strong base dissolving in dilute acids and giving well-characterised salts. Its solution in concentrated sulphuric acid is colourless even after the addition of a crystal of potassium nitrate. This reaction distinguishes tetrahydroprotoberberine from other alkaloids of this series, for the sulphuric acid solutions of all those containing methoxy- or methylenedioxy-groups develop coloration under these conditions. The colours are probably

due to nitration occurring in the nuclei activated by these substituent groups.

Tetrahydroprotoberberine hydrochloride is readily soluble in water, from which it separates in slender needles, m. p. 232° (Found: C, 75·4; H, 6·8. $C_{17}H_{18}NCl$ requires C, 75·1; H, 6·6%), and very sparingly soluble in dilute hydrochloric acid. The still more sparingly soluble, crystalline *hydriodide* separates when a solution of sodium iodide is added to the aqueous solution of the hydrochloride. The *picrate* crystallises in small yellow needles, m. p. 151°, when an alcoholic solution of the base is mixed with picric acid; it is soluble in glacial acetic acid or hot alcohol, sparingly soluble in cold alcohol, and almost insoluble in water (Found: C, 59·0; H, 4·6. $C_{23}H_{20}O_7N_4$ requires C, 59·5; H, 4·3%).

The Protoberberinium Salts (as V).—Tetrahydroprotoberberine, dissolved in the minimum of boiling alcohol, was mixed with anhydrous sodium acetate, and an alcoholic solution of iodine added until a permanent colour remained. The dark brown, granular precipitate of the *periodide* was collected, washed well with water, suspended in water, decomposed with sulphur dioxide, and the resulting yellow *iodide* recrystallised from boiling water; fine yellow needles, m. p. 232° (decomp.) (Found: C, 56·2; H, 4·1. $C_{17}H_{14}NI$ requires C, 56·2; H, 3·9%). The *chloride* was readily obtained when an aqueous suspension of the iodide was digested with excess of silver chloride for 2 hours on the steam-bath. After filtering, concentrating, and adding hydrochloric acid, the chloride separated as a mass of needles having only a slight yellow tinge; it was recrystallised from water and left on porous porcelain exposed to the air for 2 days. It then had the composition $C_{17}H_{14}NCl,4H_2O$, and after heating at 100° it still retained $\frac{1}{2}H_2O$ (Found: loss at 100°, 18·3. $C_{17}H_{14}NCl,4H_2O$ requires $3\frac{1}{2}H_2O$, 18·5. Found in material dried at 100°: C, 74·2; H, 5·5. $C_{17}H_{14}NCl,\frac{1}{2}H_2O$ requires C, 73·8; H, 5·4%). *Protoberberinium picrate* was obtained as yellow flocks on adding aqueous picric acid to a hot aqueous solution of the chloride; it crystallised from glacial acetic acid, in which it is sparingly soluble, in fine, yellow needles, m. p. 192—193°.

Oxyprotoberberine (VI).—A boiling solution of protoberberinium chloride (0·5 g.) in water (5 c.c.) was added to a hot solution of potassium hydroxide (2·5 g.) in a little water, and the mixture heated on the steam-bath for 3 hours; the oil which separated solidified on long standing. It was usually extracted with ether, the ether removed, and the residual gum extracted several times with very dilute hydrochloric acid. By this treatment the dihydroprotoberberine present was removed, but we were not successful

in isolating the small quantities of this substance in a pure state. The residue, insoluble in dilute hydrochloric acid, was dissolved in hot glacial acetic acid and mixed with a few drops of boiling water; *oxyprotoberberine* then gradually separated and, after a second treatment with acetic acid, it was obtained pure in slender, satiny, colourless needles, m. p. 102° (Found: C, 82·6; H, 5·5. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3%). It is rather sparingly soluble in the usual organic solvents, with the exception of glacial acetic acid, and does not dissolve in dilute mineral acids. The pale yellow solution in concentrated sulphuric acid becomes pale brown on the addition of a crystal of potassium nitrate.

Tetrahydroprotoberberine Methiodides (VII).—Tetrahydroprotoberberine (5 g.) and methyl iodide (10 c.c.) were heated under reflux for ½ hour, the excess of methyl iodide was evaporated, and the solid dissolved in boiling water (250 c.c.); the *β-methiodide*, which separated on cooling, recrystallised from water in colourless prisms, m. p. 230—232° (decomp.) (Found: C, 57·2; H, 5·4. $C_{18}H_{20}NI$ requires C, 57·3; H, 5·3%). The *α-methiodide* gradually separated from the aqueous mother-liquor in colourless nodules, and crystallised from alcohol in small needles, m. p. 212° (Found: C, 57·1; H, 5·2). The *methochloride* was obtained by heating an aqueous suspension of the mixed methiodides with silver chloride. It is very soluble in water and separates as a syrup on concentration.

Anhydromethyltetrahydroprotoberberine (VIII).—Tetrahydroprotoberberine methiodide (or methochloride) was heated with excess of 10% methyl-alcoholic potassium hydroxide for 3 hours. The mixture was diluted with water, the oily base extracted with ether, dried over potassium carbonate, filtered, and the ether removed, leaving the base as an oil which did not crystallise. When triturated with dilute hydrochloric acid, it was converted into the sparingly soluble hydrochloride, and this crystallised from water in small prisms, m. p. 234—235° (decomp.), containing water of crystallisation, which is lost at 100°, the substance falling to a fine powder (Found: C, 75·0; H, 7·0. $C_{18}H_{20}NCl$ requires C, 75·6; H, 7·0%). The same base is the only ether-soluble product obtained when tetrahydroprotoberberine methiodide is treated with silver hydroxide, and the solution evaporated in a good vacuum. The ether-insoluble residue was completely soluble in water and appeared to be undecomposed *methohydroxide*. After being boiled with aqueous methyl alcohol for 4 hours, the base (VIII) was recovered unchanged and identified by conversion into the sparingly soluble hydrochloride. It was also unchanged by boiling with chloroform for 3 hours, whilst the hydrochloride was recovered after being heated with dilute hydrochloric acid on the steam-bath for 6 hours.

We wish to thank Mr. Fred Hall for carrying out the analyses required during this and the two preceding investigations. One of us (S. N. C.) desires to thank the United Provinces Government for a Scholarship which has enabled him to take part in these researches.

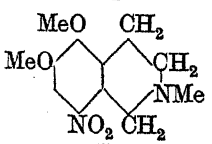
THE DYSON PERRINS LABORATORY,
OXFORD.
ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE. [*Received, August 5th*, 1927.]

CCCV.—5 : 6-*Dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-iso*quinoline and some Derivatives.*

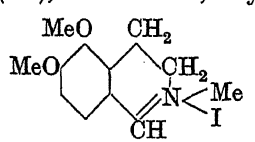
By ROBERT DOWNS HAWORTH.

THE present communication describes some experiments which were undertaken in order to discover whether the introduction of a nitro-group into a suitable position in the benzene nucleus of a 2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline derivative is capable of inducing such a reactivity in the 1-methylene group as could be utilised in synthetical work connected with the *iso*quinoline alkaloids. Suitable nitro*iso*quinoline derivatives are not readily accessible, and it has been necessary to synthesise 8-*nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (I) in order to test the above possibility.

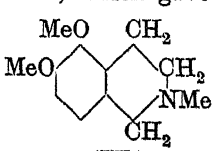
2 : 3-Dimethoxycinnamic acid, prepared by condensing 2 : 3-dimethoxybenzaldehyde with malonic acid, was converted into β-2 : 3-dimethoxyphenylpropionic acid by reduction with sodium amalgam (Perkin and Robinson, J., 1914, **105**, 2387). The *amide* of this acid was treated with sodium hypochlorite, and the resulting β-2 : 3-*dimethoxyphenylethylamine* converted into its N-*formyl* derivative, which yielded 5 : 6-*dimethoxy*-3 : 4-*dihydro*iso*quinoline* on treatment with phosphorus oxychloride. This oily base was converted to a crystalline *methiodide* (II), which was reduced by zinc dust and dilute sulphuric acid to 5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (III), a colourless, oily base, which gave a



(I.)



(II.)

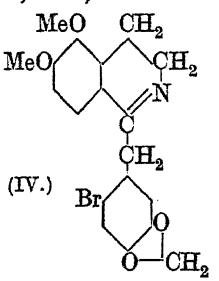


(III.)

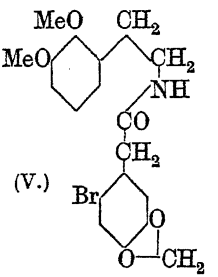
crystalline *hydriodide* and *picrate*. When this base was nitrated in glacial acetic acid it was converted into the required base (I), which,

however, did not condense with piperonal or veratraldehyde in the presence of either piperidine or methyl-alcoholic potassium hydroxide, from which it might be inferred that the effect of the nitro-group on the 1-methylene group is neutralised by the methylimino-grouping.

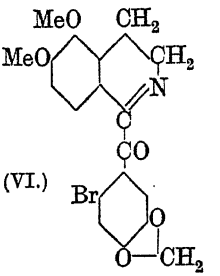
6′-*Bromo*-5:6-*dimethoxy*-3′:4′-*methylenedioxy*-1-*benzyl*-3:4-*dihydro*isoquinoline (IV) has been prepared from 3′:4′-*methylenedioxy*-6′-*bromophenylaceto*-β-2:3-*dimethoxyphenylethylamide* (V), and, like other bases of this type, it is oxidised by the air to 6′-*bromo*-5:6-*dimethoxy*-3′:4′-*methylenedioxy*-1-*benzoyl*-3:4-*dihydro*isoquinoline (VI) (compare Buck, Haworth, and Perkin, J., 1924, **125**, 2176).



(IV.)



(V.)



(VI.)

EXPERIMENTAL.

β-2:3-Dimethoxyphenylpropionic acid was prepared as follows: 2:3-Dimethoxybenzaldehyde (10 g.), malonic acid (13 g.), pyridine (25 c.c.), and piperidine (0·5 c.c.) were heated for 1½ hours on the water-bath, then boiled for ½ hour, and poured into dilute hydrochloric acid; the 2:3-dimethoxycinnamic acid was collected (yield, 95%), dissolved in 20% sodium hydroxide, and reduced at 80° with 4% sodium amalgam (200 g.). The mixture was filtered, acidified with hydrochloric acid, and the β-2:3-dimethoxyphenylpropionic acid collected and recrystallised from hot water (m. p. 68°).

β-2:3-*Dimethoxyphenylpropionamide*.—The foregoing acid (10 g.) was dissolved in chloroform (20 c.c.) and allowed to react for 1½ hours with thionyl chloride (6 c.c.) at the ordinary temperature. The mixture was poured into concentrated ammonia (50 c.c.) and water (50 c.c.), the chloroform removed by distillation, the residual liquid filtered from a little tar, and cooled; the resulting *amide* (9·5 g.) was crystallised from benzene in large, irregular prisms, m. p. 99—100° (Found: C, 62·8; H, 7·1. $C_{11}H_{15}O_3N$ requires C, 63·1; H, 7·2%), readily soluble in ether, alcohol, and hot water or benzene, but sparingly soluble in petroleum ether.

β-2:3-*Dimethoxyphenylethylamine*.—The amide (10 g.) was shaken with a solution of sodium hypochlorite, prepared by absorbing

chlorine (from 33 g. of potassium permanganate and concentrated hydrochloric acid) in 10% sodium hydroxide (100 c.c.). When it had dissolved, the temperature was raised to 70° for 1 hour, the solution cooled, treated with sodium hydroxide (90 g.), heated to 80° for 1½ hours, cooled, thoroughly extracted with benzene, the extract dried, the benzene removed, and the residual oil (8 g.) distilled under diminished pressure. β-2 : 3-*Dimethoxyphenylethylamine* boils at 190°/70 mm. (Found: C, 66·5; H, 8·4. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%).

The *hydrochloride* is very soluble in water or alcohol, and separates as an oil on the addition of ether to the alcoholic solution. The *picrate*, prepared in alcoholic solution, crystallised from alcohol in yellow plates, m. p. 174—176° (Found: C, 47·1; H, 4·5. $C_{16}H_{18}O_9N_4$ requires C, 46·8; H, 4·4%).

5 : 6-*Dimethoxy*-3 : 4-*dihydroisoquinoline Methiodide* (II).—The above amine (10 g.) and anhydrous formic acid (7 g.) were heated at 180—200° for 3 hours. The resulting N-*formyl* derivative was dissolved in toluene (50 c.c.), phosphorus oxychloride (30 c.c.) added, and the mixture boiled for 1 hour; it was then diluted with petroleum ether (b. p. 40—60°), the solvent decanted from the brown gum, the latter dissolved in a little alcohol, poured into dilute hydrochloric acid, and non-basic impurities were extracted with benzene. The acid layer was made alkaline with sodium hydroxide, extracted with benzene, the extract dried over potassium carbonate, and the benzene removed, leaving 5 : 6-*dimethoxy*-3 : 4-*dihydroisoquinoline* (5 g.) as an oil which did not crystallise, but which dissolved completely in dilute hydrochloric acid to a pale yellow solution. The oil was boiled under reflux with methyl iodide, excess of the latter was removed by distillation, and the solid *methiodide* dissolved in methyl alcohol and precipitated by ether; pale yellow needles, m. p. 174—175° (Found: C, 43·3; H, 4·9. $C_{12}H_{16}O_2NI$ requires C, 43·2; H, 4·8%). This methiodide is very soluble in water and in methyl and ethyl alcohols, the yellow solutions possessing a green fluorescence.

5 : 6-*Dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (III).—The methiodide (II) (2 g.) was dissolved in dilute sulphuric acid, heated with excess of zinc dust on the water-bath until the solution became colourless, and filtered; the filtrate was made alkaline with ammonia, the oily base extracted with chloroform, the extract dried over potassium carbonate, and the solvent removed, whereby the *base* (III) was obtained as an oil which did not solidify on long standing. The *hydrochloride* was very soluble in water or alcohol. The *hydriodide* was obtained by adding potassium iodide to a solution of the base in dilute hydrochloric acid and recrystallising the

precipitated solid from ethyl alcohol; colourless nodules, m. p. 201° (decomp.) (Found: C, 43·2; H, 5·5. $C_{12}H_{18}O_2NI$ requires C, 43·0; H, 5·4%). The *picrate* separates from alcohol in yellow needles, m. p. 164° (decomp.).

8-*Nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (I).—A solution of the tetrahydro-base (1 g.) in glacial acetic acid (25 c.c.) was treated with concentrated nitric acid (2 c.c.) in acetic acid (5 c.c.) containing urea, the temperature being maintained below 20° for 4 hours. The nitration mixture was diluted with water, made alkaline with ammonia, the buff-coloured nitro-compound collected, and crystallised from aqueous methyl alcohol; almost colourless prisms, m. p. 104—105° (Found: C, 57·1; H, 6·4. $C_{12}H_{16}O_4N_2$ requires C, 57·2; H, 6·3%). The 8-*nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline is readily soluble in the usual organic solvents, and gradually turns green on exposure to light. It was reduced with zinc dust and hydrochloric acid and filtered; the addition of ferric chloride then produced a blue coloration. Numerous unsuccessful attempts were made to condense this base with piperonal or veratraldehyde under a variety of conditions, piperidine and alcoholic potassium hydroxide being used as catalysts.

6′-*Bromo*-3′ : 4′-*methylenedioxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide* (V) was obtained by heating molecular proportions of β-2 : 3-dimethoxyphenylethylamine and 6-bromohomopiperonylic acid at 180° for 1½ hours. The *amide* crystallised from ethyl alcohol in colourless needles, m. p. 131° (Found: C, 53·9; H, 4·8. $C_{19}H_{20}O_5BrN$ requires C, 54·0; H, 4·7%).

6′-*Bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline (IV) was prepared by boiling the amide (V) (5 g.) for 1½ hours with phosphorus oxychloride (15 c.c.) and toluene (25 c.c.), adding petroleum ether, and decanting the solvents from the gum. The latter was dissolved in dilute sulphuric acid, filtered from tarry material, and made alkaline with sodium hydroxide; the oily base which separated rapidly hardened, and was collected, washed with water, and crystallised from ethyl alcohol; rhombic plates, m. p. 134—135° (Found: C, 55·9; H, 4·6. $C_{19}H_{18}O_4NBr$ requires C, 56·4; H, 4·5%). Alcoholic solutions of this base were slowly oxidised on exposure to the air to 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*-3-4-*dihydro*isoquinoline (VI), which crystallises from alcohol in colourless warts, m. p. 168° (Found: C, 54·7; H, 4·1. $C_{19}H_{16}O_5NBr$ requires C, 54·5; H, 3·8%), and gives an intense green coloration on being warmed with acetic anhydride.

THE UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, August 9th*, 1927.]

CCCVI.—*Investigations on the Bivalency of Carbon. Part I. The Displacement of Chlorine from Diphenylchloromethane. s-Tetraphenyldimethyl Ether.*

By Allan Miles Ward.

The formation of *s*-tetraphenyldimethyl ether on boiling diphenylbromomethane with water was explained by Nef (*Annalen*, 1897, **298**, 234) on the assumption that the reaction proceeded through a phase involving bivalent carbon:

$$CHPh_2Br \xrightarrow{-HBr} CPh_2< \xrightarrow{H_2O} CHPh_2\cdot OH$$
$$\qquad\qquad\qquad\quad \Big| \xrightarrow{CHPh_2\cdot OH} (CHPh_2)_2O$$

If this be so, the same considerations as those advanced for α-chloroethylbenzene (Ward, this vol., p. 445) should apply to the velocity coefficients for the displacement of the halogen atom from diphenylchloromethane. Thus the rates of displacement of the chlorine should be uninfluenced by the presence or the absence of sodium hydroxide. This is now shown to be the case for aqueous (10% by vol.) ethyl-alcoholic solutions at 25°. When sodium hydroxide is present in a concentration equivalent to the diphenylchloromethane, the velocity coefficient is that of a unimolecular reaction and of the same value as when sodium hydroxide is absent. When the concentration of the sodium hydroxide is doubled, the reaction remains unimolecular, but the velocity is somewhat decreased. A similar observation is recorded by Senter and Tucker (J., 1916, **109**, 697) for the reaction between water and the phenylbromoacetate ion.

In ethyl-alcoholic solution without added water, the presence of sodium ethoxide produced no change in the velocity of the displacement of the halogen (it was unnecessary for the alcohol to be completely anhydrous in these experiments, and lime-dried material was therefore used throughout); the presence of sodium hydroxide caused a considerable increase in the rate at 25·0°, but the reaction remained unimolecular. Observations at 35·0° in the presence and in the absence of sodium hydroxide showed similar differences, but the temperature coefficients calculated from the two sets of results were in agreement. With increasing concentration of water, the velocity of the reaction increased, being about 30 times as great when 20% of water was present as in the absolute-alcoholic solution. In the previous communication on α-chloroethylbenzene (*loc. cit.*), all velocity measurements were made in 20% aqueous-alcoholic solutions, and comparison with the velocity coefficients

of the present reaction under similar conditions shows that the halogen is displaced some 166 times more rapidly from $CHPh_2Cl$ than from CHPhMeCl.

In the kinetic experiments, the products from diphenylchloromethane were benzhydrol and diphenylmethyl ethyl ether. These conclusions are based on (1) a Zeisel determination on the products, and (2) the reaction between the products and hydrogen chloride, whereby diphenylchloromethane is re-formed from both benzhydrol and diphenylmethyl ethyl ether. In some of the experiments described, the estimation of chlorine by (2) gave low results for diphenylchloromethane, and repeated treatment with hydrogen chloride did not alter these values. In these experiments, the products were distilled at atmospheric pressure, but when all distillations were carried out under reduced pressure, the chlorine thus estimated agreed more closely with the calculated value for diphenylchloromethane. There can thus be no doubt that the low values obtained in some experiments were due to the presence of other substances formed during the distillation of the benzhydrol–diphenylmethyl ethyl ether mixture. Indeed, it was found by Goldthwaite (*Amer. Chem. J.*, 1903, **30**, 461) that *pp'*-dibromodiphenylmethyl ethyl ether on being heated at 300° decomposed entirely to *pp'*-dibromodiphenylmethane and *pp'*-dibromobenzophenone, together with a lower-boiling fraction, probably ethyl alcohol, and a gas, possibly ethylene. Bacon (*ibid.*, 1905, **33**, 92) obtained benzophenone, tetraphenylethane, and acetaldehyde on submitting diphenylmethyl ethyl ether to similar treatment. Nef (*loc. cit.*, p. 236) had previously observed that benzhydrol at 300° decomposes completely to diphenylmethane, benzophenone, and tetraphenylethane. The analytical results would point, however, to the decomposition of the ether being very much less at atmospheric pressure than that of the benzhydrol. The Zeisel determinations are of interest in showing that some 8% of benzhydrol is formed when lime-dried alcohol is used, this no doubt being due to the water present in this solvent. In aqueous (10% by vol.) ethyl-alcoholic solution, the proportion of benzhydrol formed is higher in the absence of sodium hydroxide than in its presence, being 18% and 14%, respectively, and this provides further evidence that hydroxyl ions are not directly active in the substitution.

The reaction mechanism derived from the kinetic results and from the products of reaction may thus be stated

$$CHPh_2Cl \longrightarrow CPh_2< + HCl \text{ (slow)}$$
$$CPh_2< + H_2O \longrightarrow CHPh_2{\cdot}OH \text{ (rapid)}$$
$$CPh_2< + EtOH \longrightarrow CHPh_2{\cdot}OEt \text{ (rapid)}$$

exactly as for α-chloroethylbenzene, and no experimental results are obtained contrary to Nef's hypothesis that the reaction proceeds through the phase $CPh_2<$.

It is shown also that *s*-tetraphenyldimethyl ether may be formed with ease from benzhydrol by boiling it under reflux with hydrochloric acid, just as, under similar conditions, αα′-diphenyldiethyl-ether and styrene are formed from phenylmethylcarbinol (Ward, *loc. cit.*). If the former reaction proceeds through the phase $CPh_2<$ as postulated, no unsaturated hydrocarbon of the styrene type could be formed, and the ether was, in fact, the only product isolated. The effects of varying the times of heating at 100° and of altering the concentration of hydrochloric acid were observed in relation to the proportion of ether formed. With increasing concentration of hydrochloric acid, the proportion of ether formed passed through a maximum, and the amount of diphenylchloromethane increased from zero at first, until, with concentrated acid, it became the main product of reaction. Conversely, when *s*-tetraphenyldimethyl ether was boiled with concentrated hydrochloric acid, diphenylchloromethane was the main product, whereas with *N*/2-acid no change occurred. Moreover, it was found in these experiments that when the products were distilled and then treated with hydrogen chloride, values for the chlorine content were obtained which were too low for diphenylchloromethane. This was doubtless due to the decomposition of the original products of reaction on distillation, as in the case of the benzhydrol–diphenylmethyl ethyl ether mixtures (p. 2286). Thus Nef (*loc. cit.*, p. 236) found that *s*-tetraphenyldimethyl ether on being heated at 300° decomposed to benzophenone, diphenylmethane, and tetraphenylethane. In the present experiments, the products of distillation were not systematically examined except in the case of one experiment with *s*-tetraphenyldimethyl ether, in which diphenylmethane was isolated. The presence of this as a product of secondary decomposition would account for the anomalous chlorine results. When the products of the reaction between concentrated hydrochloric acid and benzhydrol or *s*-tetraphenyldimethyl ether were examined by methods avoiding distillation or heating at higher temperatures, no evidence was obtained for the formation of any substances other than diphenylchloromethane, benzhydrol, and *s*-tetraphenyldimethyl ether.

Although the results find a complete explanation on the basis of Nef's hypothesis, other interpretations may possibly be formulated. Thus assuming that diphenylchloromethane reacts in virtue of its ions as in (1)—(4), the kinetic results would then necessitate

that (1) should be a time reaction and (2) and (3) extremely rapid.

$$(1)\ CHPh_2Cl \longrightarrow CHPh_2^{\cdot} + Cl'$$
$$(2)\ CHPh_2^{\cdot} + OH' \longrightarrow CHPh_2{\cdot}OH$$
$$(3)\ CHPh_2^{\cdot} + OEt' \longrightarrow CHPh_2{\cdot}OEt$$
$$(4)\ CHPh_2^{\cdot} + OCHPh_2' \longrightarrow (CHPh_2)_2O$$

Although an increase in the hydroxyl-ion concentration from about 10^{-8} (in 10% aqueous ethyl-alcoholic solution) to 0·176 (in the presence of sodium hydroxide) would thus greatly increase the velocity of (2), it would not affect the measured velocity, which *ex hypothesi* depends solely on (1). Also, from the equilibrium $EtOH + OH' \rightleftharpoons OEt' + H_2O$, an increase is seen to take place in the ethoxyl-ion concentration parallel with that in the hydroxyl-ion concentration, but the increased velocity of (3) would not influence the measurable velocity. Slowness of (1) and rapidity of (2) and (3) would be almost inevitably connected, since each represents the very slight tendency for the formation of $CHPh_2^{\cdot}$ ions. The same considerations hold concerning phenylmethylcarbinol (*loc. cit.*). Should the reaction in this case proceed through the phase CHPhMe$^{\cdot}$, it must be assumed that this is capable of losing a hydrogen ion in order to account for the production of styrene. The halogen displacement from the triarylmethyl chlorides may be assumed to take place as in (1), but the hexaaryldimethyl ethers have not been prepared by this method (compare Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 200). In this connexion an examination of systems of the type $CR_1R_2R_3Cl$ should provide valuable data.

Experimental.

Diphenylchloromethane was prepared from benzhydrol by means of hydrogen chloride in benzene solution (Böeseken, *Rec. trav. chim.*, 1903, **22**, 313; Montagne, *ibid.*, 1906, **25**, 405) and was obtained as a colourless liquid, b. p. 158·5—159·5°/12 mm., which solidified to a colourless solid, m. p. 20·5° (Engler and Berthge, *Ber.*, 1874, **7**, 1128, give m. p. 14°, and Böeseken gives m. p. 12—14°). It was kept in small sealed glass tubes, for turbidity developed rapidly in contact with the atmosphere. The chlorine was determined (i) by heating a weighed sample in aqueous ethyl alcohol and titrating the liberated acid with standard alkali until the colour change of the indicator (phenolphthalein) was permanent (Found : Cl, 17·64. Calc. : Cl, 17·53%), and (ii) by Stepanow's method (Found : Cl, 17·47%). In all subsequent analyses, the chlorine was estimated as under (i).

Diphenylchloromethane was also prepared by suspending *s*-tetraphenyldimethyl ether (90 g.) in benzene (180 c.c.) and passing in a rapid stream of hydrogen chloride for 1 hour at room temperature. The ether dissolved completely and an aqueous layer formed; this was separated and the benzene solution dried by means of calcium chloride. The hydrogen chloride was removed in a current of carbon dioxide, and the product, b. p. 165·5°/15 mm., collected; yield, 88 g. (Found: Cl, 17·57%). Some tar remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane and Ethyl Alcohol.—(*a*) Ethyl alcohol (250 c.c.), dried by refluxing and distilling over quick-lime, was added to diphenylchloromethane (5 g.). The solution was maintained at 25° for 5 days, free hydrogen chloride was then removed by means of potassium carbonate, and the alcoholic solution fractionated, 4·9 g. of liquid, b. p. 146—147°/9 mm., being obtained (Nef, *loc. cit.*, p. 234, gives b. p. 153°/15 mm. for diphenylmethyl ethyl ether) (Found: OEt, 19·6. Calc. for diphenylmethyl ethyl ether: OEt, 21·2%). The product redistilled at 281°/766 mm. (Kostanecki and Lampe, *Ber.*, 1906, **39**, 4019, give b. p. 288°) (Found: OEt, 19·2%).

(*b*) Repetition of this experiment with 15 g. of diphenylchloromethane and 500 c.c. of alcohol for 10 days gave 14·2 g., b. p. 115—119°/4 mm. (Found: OEt, 19·5, 19·4%).

(*c*) Hydrogen chloride was passed through the liquid obtained in (*a*) at room temperature. Considerable heat was developed, and after some time separation into two layers took place. Calcium chloride was added, and after standing, the products, which remained heterogeneous, were distilled. On heating, appreciable charring and marked evolution of gas took place, the material then distilling smoothly, b. p. 156—158°/11 mm. (Found: Cl, 16·1. Calc. for diphenylchloromethane: Cl, 17·53%).

(*d*) 5 G. of the product from (*b*) were dissolved in benzene (15 c.c.) and hydrogen chloride was passed in rapidly for 2 hours. Two layers were again formed and remained after drying by means of calcium chloride. The hydrogen chloride was removed in a stream of carbon dioxide, the benzene distilled under diminished pressure, and a colourless liquid obtained (4·2 g.), b. p. 120—121°/3 mm. (Found: Cl, 17·25%). Considerable dark brown gum remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane with Aqueous Ethyl Alcohol.—(*e*) A solution of diphenylchloromethane (5 g.) in ethyl alcohol (225 c.c.) and water (25 c.c.) was kept at 25° for 12 hours, the water then removed by means of potassium carbonate, and the products distilled, giving 4·5 g. of liquid, b. p. 113—120°/3

mm., which redistilled at 281—288°/766 mm. (Found : OEt, 17·8%), some charred material remaining in the distilling flask. The liquid was dissolved in petroleum ether and treated with hydrogen chloride as under (*c*) above, a fraction of b. p. 162—163°/16 mm. (Found : Cl, 16·58%) being obtained.

(*f*) Ethyl alcohol (1125 c.c.), water (125 c.c.), and diphenylchloromethane (25 g.) were treated as in (*b*) and gave 21·5 g., b. p. 125—130°/3 mm. (Found : OEt, 17·3, 17·4%). Treatment of a sample (5 g.) as under (*d*) above, gave 4·4 g. of colourless liquid, b. p. 115°/1 mm. (Found : Cl, 17·22%). Some gum remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane with Aqueous Ethyl-alcoholic Sodium Hydroxide.—(*g*) Diphenylchloromethane (5 g.) was dissolved in ethyl alcohol (225 c.c.) and aqueous 1·76*N*-sodium hydroxide (25 c.c.). The solution was kept at 25° for 12 hours, dried, and the liquid distilled, b. p. 116—124°/3 mm.; yield, 4·3 g. The products redistilled at 279—285°/766 mm. (Found : OEt, 18·2%). After treatment with hydrogen chloride in benzene solution, the liquid distilled at 156—158°/11 mm. (Found : Cl, 16·6%). This product was again treated with hydrogen chloride, but the chlorine content remained unchanged.

(*h*) The water in Expt. (*f*) was replaced by the same volume of aqueous 2*N*-sodium hydroxide and the same procedure followed; yield, 21·5 g.; b. p. 114—121°/3 mm. (Found : OEt, 18·2, 18·1%). A small amount of gum remained in the distilling flask. Treatment of a sample (5 g.) as under (*d*) above, gave 4·3 g. of a colourless liquid, b. p. 121—124°/4 mm. (Found : Cl, 17·29%). A small amount of brown oil remained in the distilling flask.

Reaction between Benzhydrol and Hydrochloric Acid.—In each experiment benzhydrol (5 g.) and hydrochloric acid of the normality stated were heated in a pressure flask immersed in a bath of boiling water for the times shown in the following table. The products solidified on being poured into cold water, and the *s*-tetraphenyldimethyl ether and benzhydrol were then readily separated by dissolving the mixture in hot alcohol, the main bulk of the ether crystallising in a pure condition on cooling. Addition of a little water to the alcoholic mother-liquor precipitated a mixture of the ether and benzhydrol, which was separated into its components by a repetition of this process, whilst by the addition of the aqueous alcoholic solution to excess of water, the benzhydrol was obtained in a pure condition. The purity of the benzhydrol (m. p. 68°) and of the *s*-tetraphenyldimethyl ether (m. p. 110°) was checked in these and in all subsequent experiments by determining the m. p.'s both alone and when mixed with authentic specimens. In the

HCl, *N*.	Time (hrs.).	Yields, g. Ether.	Benzhydrol.	HCl, *N*.	Time (hrs.).	Yields, g. Ether.	Benzhydrol.
0·5	1	—	5·0	1	6	2·1	2·3
0·5	4	1·2	3·5	2	1	1·55	3·0
0·5	8	1·75	2·85	2	6	3·5	0·75
0·5	20	2·55	2·4	3·5	1	3·6	0·95
1	1	0·8	4·05	3·5	6	3·9	—

final experiment, no precipitate but only a turbidity was formed on adding the aqueous alcoholic solution to excess of water. In several of the preceding experiments, mainly those in which the higher concentrations of acid were used or in which the times of heating were longer, the total yield of ether and carbinol was lower than the theoretical, and in these cases the filtrate after separation of the benzhydrol was turbid, doubtless due to the partial formation of diphenylchloromethane, as shown in the following experiments.

(*i*) Benzhydrol (5 g.) and 5*N*-hydrochloric acid (75 c.c.) were heated in a pressure flask at 100° for 1 hour. The products on being poured into cold water solidified to a pasty mass. On the addition of petroleum ether (b. p. 40—60°), a white solid was at once obtained, which on crystallisation from alcohol gave *s*-tetraphenyldimethyl ether (2·2 g.). Dilution of the alcoholic filtrate with water produced a turbidity only. The petroleum-ether solution was dried, and the solvent evaporated completely at room temperature, a pasty mass (2 g.; Cl, 7·7%) thus being obtained.

(*j*) Benzhydrol (10 g.) was boiled under reflux with concentrated hydrochloric acid (100 c.c.) for 2 hours. The oil, which did not solidify on cooling, was extracted with ether, dried and distilled; b. p. 160—161°/15 mm.; yield, 7·85 g.; Cl, 15·4%. A black gum remained in the distilling flask. In a second experiment, with only 1 hour's boiling, the following results were obtained: b. p. 159—161°/14 mm.; yield 7·6 g.; Cl, 15·2%; whilst in a third experiment, the reaction being carried out in a pressure flask immersed in a bath of boiling water for 1 hour, 7·4 g. of product (Cl, 14·9%) were obtained. This was dissolved in benzene, saturated with hydrogen chloride, and on distillation gave a liquid, b. p. 156—158°/12 mm. (Cl, 14·7%).

(*k*) Benzhydrol (50 g.) was boiled under reflux with concentrated hydrochloric acid (500 c.c.) for 2 hours. The cooled products were extracted with ether, dried, and the ether distilled under diminished pressure at room temperature. The oil (50 g.; Cl, 15·3%) so obtained was dissolved in some 250 c.c. of petroleum ether (b. p. 40—60°), but no solid separated on standing. The petroleum ether was completely removed by distillation at room temperature, excess of water added, and the mixture maintained at 25° for 3 weeks with

occasional shaking. The displacement of the halogen at the end of this period was still incomplete, and the mixture was therefore gently warmed until no further acidity developed. On cooling, the products solidified to a hard mass, which was filtered, washed with water, and dried (yield 45·5 g.). Crystallisation from petroleum ether gave a crop of 41·6 g., yielding benzhydrol (20·9 g.) and *s*-tetraphenyldimethyl ether (20·3 g.). From the petroleum-ether liquors on evaporation at room temperature a solid (3·35 g.) was obtained; on recrystallisation from petroleum ether, this gave a product (2·5 g.) which was separated into benzhydrol (0·8 g.) and *s*-tetraphenyldimethyl ether (1·6 g.). The residual liquors on evaporation at room temperature gave a small amount of solid, from which 0·1 g. of the ether was separated, and a yellow oil (*ca.* 0·5 c.c.) which completely decomposed on attempted distillation.

Reaction between s-*Tetraphenyldimethyl Ether and Hydrochloric Acid.*—(*l*) *s*-Tetraphenyldimethyl ether (10 g.) and *N*/2-hydrochloric acid (150 c.c.) were boiled under reflux for 8 hours. Solid was present all the time and 9·9 g. of ether were recovered.

(*m*) *s*-Tetraphenyldimethyl ether (50 g.) and concentrated hydrochloric acid (500 c.c.) were boiled under reflux for 1 hour. The products were cooled, extracted by ether, dried, and the solvent was removed on the water-bath. During the heating, the liquid darkened considerably (Found: Cl, 6·54%). The products on inoculation with *s*-tetraphenyldimethyl ether solidified to a stiff paste, which was filtered and washed with petroleum ether (b. p. 40—60°), *s*-tetraphenyldimethyl ether (10·5 g.) being thus obtained pure. The filtrate was distilled under diminished pressure, b. p. 145—170°/12 mm.; yield 25 g. (Found: Cl, 10·5%). A considerable amount of dark brown gum remained in the distilling flask, but the only product which was separated from this was *s*-tetraphenyldimethyl ether (1·7 g.). The above distillate (25 g.) was boiled with water for ½ hour (reflux), but remained liquid on cooling. Addition of petroleum ether yielded a solid (6·7 g.) which gave benzhydrol (5·9 g.) and *s*-tetraphenyldimethyl ether (0·4 g.). The petroleum-ether solution was dried and distilled; b. p. 146—160°/14 mm.; yield, 10 g. A considerable amount of oil, which solidified to a hard mass, remained in the distilling flask, and this on crystallisation from alcohol gave *s*-tetraphenyldimethyl ether (3 g.). Phenylhydrazine (7 g.) and alcohol (20 c.c.) were added to the distillate (10 g.) and the solution was refluxed for 9 hours, but even on cooling it remained homogeneous, thus showing benzophenone to be absent. Excess of dilute hydrochloric acid was added and the products were distilled in steam; a pleasant-smelling oil was obtained, which was extracted with ligroin, dried, and distilled,

giving fractions (1) b. p. 129—135°/11 mm., 2 c.c.; (2) b. p. 135—155°/11 mm., 4 c.c.; a small amount of liquid remained. An authentic specimen of diphenylmethane distilled at 129—130°/11 mm., and remained liquid for a considerable time after distillation, but on seeding solidified to a hard mass of long, colourless needles. Fraction (1) was similarly treated, and its behaviour was identical.

(*n*) *s*-Tetraphenyldimethyl ether (50 g.) and concentrated hydrochloric acid (500 c.c.) were boiled under reflux for 4 hours. The cooled products were extracted by ether, dried, and the solvent was removed under diminished pressure at room temperature during 7 hours; yield 47·5 g. (Found: Cl, 12·4%). The addition of petroleum ether caused a colourless solid (6·2 g.) to separate on standing, giving *s*-tetraphenyldimethyl ether (5·7 g.) and benzhydrol (0·25 g.). The petroleum ether was removed under diminished pressure at room temperature, and the colour of the products darkened, although to a very much less degree than in the preceding experiment; yield, 40·5 g. (Found: Cl, 14·2%). The replacement of the halogen was carried out exactly as in the corresponding benzhydrol experiment, a colourless, crystalline solid (37 g.) being obtained. On crystallisation from light petroleum, this gave a crop (31 g.) which yielded *s*-tetraphenyldimethyl ether (11 g.) and benzhydrol (19·5 g.). On evaporation of the liquors at room temperature a pasty solid was formed, which was washed with petroleum ether; 3·5 g. remained, yielding 3·3 g. of *s*-ether. The liquors on evaporation gave 2·3 g. of oil, which, since it still contained diphenylchloromethane, was boiled with water; on cooling, it solidified to a pasty solid, from which were separated *s*-ether (0·7 g.) and benzhydrol (0·8 g.), whilst the distillate from the small quantity of residual oil was insufficient for further examination.

Kinetic Experiments.

In the following experiments, a weighed amount of diphenylchloromethane was dissolved in ethyl alcohol (prepared by refluxing and distilling commercial absolute alcohol over quick-lime); the required amounts of water (by volume) and of sodium hydroxide or sodium ethoxide solutions were added, at the temperature of experiment, and the volume in each case was made up to 100 c.c. with ethyl alcohol. The method of experiment was that described previously (*loc. cit.*, p. 455) and the results are expressed as before, except that titrations refer to 10 c.c. of solution against alcoholic sodium hydroxide ($N/20$) or alcoholic benzoic acid ($N/20$). In each case k is calculated from the formula $k = 2{\cdot}3/t \,.\, \log_{10} a/(a - x)$ for a unimolecular reaction, t throughout being expressed in minutes, and a being based on the first titre. Typical experiments showing

the extent of the variations amongst the individual values of k are given (1 and 2), and the complete results are then summarised.

(1) Diphenylchloromethane, 0·0906 mol./l.; water, 10% (by vol.); temp. 25·0°.

t.	Titre.	k.	t.	Titre.	k.
4	1·47	—	64	15·23	0·0294
14	5·87	0·0307	84	16·60	0·0301
24	8·87	0·0294	144	17·94	—
44	13·01	0·0296	1350	18·09	—

(2) Diphenylchloromethane, 0·0818 mol./l.; sodium hydroxide, 0·0880 mol./l.; water, 10% (by vol.); temp. 25·0°.

t.	Titre.	k.	t.	Titre.	k.
3	15·98	—	63	3·46	0·0301
13	12·32	0·0280	83	2·46	0·0291
23	9·40	0·0289	279	1·06	—
43	5·62	0·0294	1260	1·00	—

(3) Temp. 25·0°.

$CHPh_2Cl$ (mol./l.).	Water (% by vol.).	NaOH (mol./l.).	NaOEt (mol./l.).	k.
0·0696	—	—	—	0·00341
0·0781	—	—	—	0·00349
0·0974	—	—	0·1297	0·00345
0·1167	—	—	0·2407	0·00354
0·1059	—	—	0·2315	0·00343
0·0733	—	0·0914	—	0·00395
0·0764	1	—	—	0·00468
0·0956	2	—	—	0·00638
0·1054	5	—	—	0·0115
0·0906	10	—	—	0·0298
0·0776	10	—	—	0·0294
0·0818	10	0·0880	—	0·0291
0·0811	10	0·0880	—	0·0293
0·0878	10	0·1760	—	0·0272
0·0845	10	0·1760	—	0·0277
0·0795	20	—	—	0·103

(4) Temp. 35·0°.

$CHPh_2Cl$ (mol./l.).	Water (% by vol.).	NaOH (mol./l.).	k.	Temp. coeff. (10°).
0·0828	—	—	0·0101	
0·0867	—	—	0·0101	2·98
0·1942	—	—	0·0104	
0·0980	—	0·0982	0·0117	2·95
0·0818	—	0·1848	0·0116	

Summary.

(1) The displacement of the halogen from diphenylchloromethane at 25° in ethyl-alcoholic solution (lime-dried) and in aqueous ethyl-alcoholic solutions, both alone and in the presence of sodium hydroxide, yields a mixture of diphenylmethyl ethyl ether (main product) and benzhydrol.

(2) The velocity coefficients obtained for this displacement in ethyl-alcoholic solution alone, and also in the presence of sodium hydroxide and of sodium ethoxide, at 25° and at 35°, are those of a unimolecular reaction, the sodium hydroxide, sodium ethoxide, or their ions playing no direct part in the halogen displacement. Similar results are obtained in aqueous-alcoholic solutions.

(3) Benzhydrol gives *s*-tetraphenyldimethyl ether in good yield on being boiled with dilute hydrochloric acid. With increasing concentration of acid, the yield of *s*-tetraphenyldimethyl ether passes through a maximum, and the yield of diphenylchloromethane rises, becoming the main product of the reaction when concentrated acid is used.

(4) *s*-Tetraphenyldimethyl ether is unchanged on boiling with *N*/2-hydrochloric acid, but with concentrated acid it is largely converted to diphenylchloromethane. Diphenylchloromethane may be prepared readily in a pure condition and in good yield by the action of hydrogen chloride on *s*-tetraphenyldimethyl ether suspended in benzene.

(5) The experimental evidence under (1), (2), (3), and (4) is in accordance with the hypothesis of Nef that the reactions proceed through a phase $CPh_2<$, in which but two groups are momentarily attached to carbon. An alternative mechanism involving the $CHPh_2^{\cdot}$ ion is also discussed.

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BIRKBECK COLLEGE,
UNIVERSITY OF LONDON, E.C. 4. [*Received, August 5th*, 1927.]

CCCVII.—*The Determination of Dissociation Constants of Dihydric Mono- and Di-nitrophenols Electrometrically and Colorimetrically.*

By FRANK LATHE GILBERT, FRANK C. LAXTON, and EDMUND B. R. PRIDEAUX.

THE conductivities were determined by the Kohlrausch method in a gas-regulated thermostat which was maintained at 25·0° ± 0·05°. The cell constant, as determined by solutions of *N*/10- and *N*/100-potassium chloride and saturated calcium sulphate, was 0·298. The conductivity water had a specific resistance of 4—5 × 10^{-6} reciprocal ohm. The conductivities were corrected for that of the water by the usual method (Ostwald and Luther, "Physico-

chemical Measurements") at the highest dilutions, when necessary. The trustworthiness of the apparatus was tested by determining the conductivity of acetic acid, with the following results:

At v =	16	32	64	128	256
$K \times 10^6$ =	18·33	18·56	18·47	18·36	18·50

The colorimetric measurements were carried out in a small colour comparator, in daylight, and in the manner already described (J., 1924, **125**, 2110; 1925, **127**, 2499).

The Preparation and Properties of the Compounds, and the Determination of their Constants.

2 : 6-*Dinitroquinol.*—The preparation and properties of this compound have already been described (J., 1924, **125**, 2110). The dissociation constant determined by Bader (*Z. physikal. Chem.*, 1890, **6**, 287), when multiplied by 10^{-2} in order to render it comparable with the more usual mode of expression, was $0{\cdot}7 \times 10^{-4}$, at dilutions from 200 to 1600. Bader's value of λ_0, translated into modern units, is 376, whereas we find that λ_0 of the dinitro-acid is 380. It was decided to repeat the measurements of this compound for this reason and for others, among which were the circumstances that it was evidently sensitive to catalytic oxidation and that the purity of some of Bader's preparations had been questioned by subsequent workers (*e.g.*, Walker and Cormack, J., 1900, **77**, 5).

Solutions freshly made from the calculated weights of either the hydrated or the anhydrous compound were found to have the same conductivities. When they were allowed to stand in contact with the electrodes for some time, the colour changed from red to yellowish-brown, the conductivity altered, and the characteristic purple colour then no longer appeared on the addition of alkali. These changes are probably due to oxidation. The colour also changed when hydrogen was passed over the electrode, and finally a black precipitate appeared; thus reduction also probably takes place. Solutions were freshly made for each determination of conductivity, the dilutions being performed outside the cell, because it was soon evident that these changes in their first stages were accompanied by a diminution in the resistance in the more dilute, as well as in the more concentrated, solutions. Three independent series of measurements were first made, and the constants calculated in the usual manner.

	First series.				Second series.			Third series.	
v =	184	368	736	1472	203	406	812	562	1124
λ =	60·2	70·0	81·8	101	66·6	76·8	85·8	74	93·2
$K \times 10^4$ =	1·62	1·13	0·80	0·655	1·83	1·26	0·81	0·83	0·71

In the fourth series, measurements were made after 20, 40, and 60 secs., and the readings were extrapolated to zero time; for instance, in one case the resistances of the solution in the cell were 1975, 1940, and 1920 ohms, respectively. Hence, at zero-time the resistance was 2010 ohms and the constant $1{\cdot}72 \times 10^{-4}$.

v =	221	442	884	1768
λ =	67·2	80	89·5	106·5
α =	0·177	0·211	0·236	0·280
$K \times 10^4$ =	1·72	1·27	0·824	0·614

There is thus an undoubted diminution of the constant with dilution, in the direction usually observed in the case of acids of medium strength, although 2 : 6-dinitroquinol is not sufficiently strong to be included in this class, which might, however, include the strongest of the acids investigated. In the case of 2 : 6-dinitroquinol, we suspect that the anomalous behaviour is connected with the transition into the second, or red, quinonoid form, for, at the p_H produced by the dissociation of the compound itself in water, this transition would have proceeded to a considerable extent. Pending an explanation, we have adopted a mean constant of 1×10^{-4}, $p_K = 4{\cdot}0 \pm 0{\cdot}2$, for comparison with the other compounds.

3 : 5-*Dinitropyrocatechol.*—This compound, as previously described (J., 1925, **127**, 2499), appears as bright yellow crystals, m. p. 164°. The conductivity of the solutions did not alter on standing in contact with the electrodes. Three series of readings gave :

At v =	890	1010	1010	1780	2020	2020	3560	4040	4040
λ =	149·5	162·5	160·0	190	204	200	228	243	243·5
$K \times 10^4$ =	2·88	3·17	3·09	2·80	3·10	2·92	2·54	2·8	2·8

The mean value of K is $2{\cdot}9 \times 10^{-4}$, $p_K = 3{\cdot}54$.

2 : 4-*Dinitroresorcinol.*—2 : 4-Dinitrosoresorcinol, prepared according to the method of Fitz (*Ber.*, 1875, **8**, 631), was treated with cold concentrated nitric acid (Kostanecki and Feinstein, *Ber.*, 1888, **21**, 3121) in a freezing mixture to minimise the formation of styphnic acid, any of which was removed by shaking with a large quantity of water. The nitro-compound appeared as light yellow crystals, m. p. 142°. The solution was quite stable in contact with the electrodes. Two series of measurements were made, in each of which a distinct diminution of the constant with increasing dilution was observed. Since this is by far the strongest acid of the series, we consider that this diminution may be due to the same causes as that found in the case of acids of medium strength.

	First series.						Second series.				
v =	190	380	760	1520	3040	6080	240	480	960	1920	7680
λ =	129	162	200	236	262	265	141·5	177	215	248	273
$K \times 10^4$ =	9·22	8·43	8·47	6·74	5·05	4·70	9·29	8·47	7·73	6·44	2·69

In accordance with the usual practice, we have excluded values

obtained at a degree of primary ionisation greater than 0·5 ($v > 700$). The mean value of K is $8{\cdot}85 \times 10^{-4}$, $p_K = 3{\cdot}05$.

The compound is colourless in acid solution, and full yellow from about p_H 6·65. There is no further colour change in more strongly alkaline solution up to p_H 12. The colorimetric degrees of transformation were investigated by the methods which are described in the two former papers (*loc. cit.*). The values were found, however, to vary with the p_H of the standard buffer solution containing the partly transformed compound, thus

At p_H =	3·69	3·37	4·2
p_K =	4·09	3·85	4·3

None of the other compounds investigated shows such variations. The colorimetric constant can therefore only be roughly defined as $3{\cdot}9 \pm 0{\cdot}4$—the mean of many determinations at various concentrations. The colour change is very gradual; thus no difference in colour between solutions of p_H 4·77 and 5·07, each containing 8 drops of $M/20$-solution of the compound (in alcohol), can be detected by visual matching.

4 : 6-*Dinitroresorcinol.*—This compound, prepared as already described (*loc. cit.*, 1925), forms yellow prisms, m. p. 214·5°. It is the least soluble of all the compounds investigated. The solutions were quite stable when in contact with the electrodes. The bridge settings were not quite so accurate at these high dilutions and resistances. The last value was not used in calculating the constant, since the corresponding degree of ionisation was 0·68.

v =	2560	5180	5180	10,360
λ =	163	198	188	257
$K \times 10^4$ =	1·22	1·09	0·94	1·39

The mean value of K is $1{\cdot}05 \times 10^{-4}$, $p_K = 3{\cdot}98$.

The solubility of the compound was found to be 0·0781 g. per litre by means of a conductivity titration, using a method which we hope to describe in a further communication.

The mobility of the dinitro-anion was determined by means of the monosodium salt. An $N/61{\cdot}9$-solution ($v_1 = 61{\cdot}9$) was diluted in steps of 2, the corresponding values of λ_1, etc., being treated by the well-known formula derived from the graph of λ and $\sqrt[3]{C}$ in order to obtain λ_0 (Kohlrausch, "Das Leitvermögen der Elektrolyte").

λ_1	λ_2	λ_4	λ_8	λ_{16}	λ_{32}
68·4	72·1	74·9	76·75	78·6	79·9

Hence $\lambda_0 = 2\lambda_8 - \lambda_1 = 85{\cdot}1$, etc.; the mean value was 85·0. The same results were also treated by the method of Ferguson and Vogel (*Phil. Mag.*, 1925, **50**, 971). In the equation

$$\log \delta\lambda = n \log C - \log B(1 - r^n),$$

in which C is the concentration, $\delta\lambda$ the difference in λ brought about by the dilution in the common ratio "r" (in this case 2), the constants n and B were found to be $n = 0{\cdot}437$, $B = 90{\cdot}9$. Hence λ_0 from the individual values of $\delta\lambda$ was 83·08 (82·8—83·2). The compound therefore behaves quite normally like a salt of a strong base and a strong acid. For several reasons we have preferred the value of λ_0 as given by the usual method. Combining this with the limiting mobility of $Na^{\cdot} = 51$, we find that of the anion to be 34, and that of the free monobasic acid 381.

Nitroquinol.—The sample consisted of dark red crystals, m. p. 128° (*loc. cit.*, 1924). The solutions, like those of dinitroquinol, changed in conductivity on standing in contact with the electrodes. Dilutions were therefore made outside the cell, and measurements were taken quickly. The two values of λ refer to two experiments at each dilution. The conductivity can be restored to nearly its original value by passing hydrogen over the electrodes.

$v =$	127	248	254	496	508
$\lambda =$	4·2 (4·74)	6·07 (6·31)	5·7 (7·25)	9·88 (10·2)	7·06 (7·74)
$K \times 10^6 =$	0·981	1·13	0·92	1·41	0·701

The values in brackets are given as showing the variability introduced by a slight delay in taking measurements. The constant is calculated from the lowest values of λ in each case. The mean constant is $1{\cdot}01 \times 10^{-6}$, $p_K = 6{\cdot}0$.

3-*Nitropyrocatechol.*—This was prepared by a modification of the method of Weselsky and Benedickt (*Monatsh.*, 1882, **3**, 386). The mixture of the 3- and 4-isomerides with unchanged pyrocatechol was distilled with steam. The distillate, containing the pyrocatechol and the 3-isomeride, was extracted with ether. The residue from this extraction was further extracted with boiling light petroleum. The 3-isomeride was obtained as bright yellow needles, m. p. 86°. Solutions kept in contact with the electrodes change in conductivity: the change is accelerated by passing oxygen and retarded by passing hydrogen. The precautions already mentioned were taken.

	First series.				Second series.	
$v =$	65·4	130·8	261·6	523·2	184	736
$\lambda =$	4·15	6·08	7·42	10·3	6·1	17·4
$K \times 10^6 =$	1·87	1·99	1·50	1·45	1·45	3·01

The mean value of K is $1{\cdot}88 \times 10^{-6}$, $p_K = 5{\cdot}73$.

The compound is colourless in acid solution, and full yellow at p_H 7·8—10·0. At higher values of p_H, there is a second change, to red-brown, becoming purple at about p_H 13—14. The colorimetric constants were determined by the methods already described:

$${}_1K = 1 \times 10^{-5},\ p_{K_1} = 4{\cdot}95;\ {}_2K_c = 0{\cdot}93 \times 10^{-11},\ p_{K_2} = 11{\cdot}03.$$

4-*Nitropyrocatechol.*—The method of Weselsky and Benedickt gives a product mixed with tarry matter. A more satisfactory method is that of Benedickt (*Ber.*, 1878, **11**, 362). The product when recrystallised from hot benzene is light brown, m. p. 173°. The conductivity of the solutions increased when they were in contact with the electrodes; the lower value of λ was therefore used in calculating the constants.

v =	48·1	51·5	96·2	192·4	384·8
λ =	1·51 (1·77)	1·72	1·97 (2·14)	2·25 (2·49)	5·22 (6·00)
$K \times 10^7$ =	3·33	4·05	2·83	1·85	5·02

The mean value of K is $3{\cdot}52 \times 10^{-7}$, $p_K = 6{\cdot}45$.

The compound is faintly yellow even in acid solution. It changes to red and ultimately to purple with increasingly alkaline solutions.

The constant of the first colour change was determined as already described. The second colorimetric constant was determined by comparison of a tube containing 5 drops at p_H 7·25 (full yellow) behind one containing 5 drops at p_H 13·76 (red) with one containing 10 drops, which matched when p_H was adjusted to 10·96. In another experiment, 8 drops of the solution of 4-nitropyrocatechol in a known p_H (10·64), were matched by 2 drops (in red solution) plus 6 (in yellow). The mean constants are $K_1 = 2{\cdot}8 \times 10^{-6}$, $p_{K_1} = 5{\cdot}56$; $K_2 = 1{\cdot}1 \times 10^{-11}$, $p_{K_2} = 10{\cdot}96$. An $M/20$-alcoholic solution was used.

2-*Nitroresorcinol.*—The method of preparation and the determination of the colorimetric constants have already been described (*loc. cit.*, 1925). The compound appeared as bright red crystals which melted sharply at 83·5°. Since the compound and its sodium salt are quite stable in solution, the latter was used in the determination of the mobility of the mononitro-anion, in the manner described above. Solutions were diluted in the cell, each dilution being two-fold, and the initial dilution, corresponding to λ_1, being 33·8.

λ_1	λ_2	λ_4	λ_8	λ_{16}	λ_{32}
66·2	69·7	72·9	75·9	77·1	78·8

Hence $\lambda_0 = 2\lambda_8 - \lambda_1 = 85{\cdot}6$, etc., the mean of the values of λ_0 being 84·9.*

* The degree of hydrolysis is inappreciable at all dilutions except the highest (v = *ca.* 1000). Taking K as $1{\cdot}6 \times 10^{-6}$, we find by the usual formula that the degree of hydrolysis is $2{\cdot}24 \times 10^{-3}$. The difference between λ_0 of sodium hydroxide and the sodium salt of the acid is $192 - 33{\cdot}5 = 158{\cdot}5$. Therefore, if these two electrolytes were equally dissociated, the repression of the hydrolysis would diminish the value of λ by

$$(2{\cdot}24 \times 10^{-3} \times 158{\cdot}5) \times 78{\cdot}8/85 = 0{\cdot}33.$$

Hence $\lambda_{32} = 78{\cdot}47$ and $2\lambda_{32} - \lambda_4 = 84{\cdot}05$.

The graph of λ against $\sqrt[3]{C}$ gives λ_0 as 84—85, and we use 84·5 as the most probable value. Hence the mobility of the anion is 33·5, and λ_0 of the free acid is 380·5. The conductivity of the acid remained constant when the solutions were kept in contact with the electrodes.

	First series.		Second and third series.			
v =	700	1400	288	349	576	1152
λ =	12·5	17·8	7·85	8·5	11·45	15·75
$K \times 10^6$ =	1·65	1·67	1·53	1·48	1·65	1·56

The mean value of K is $1{\cdot}59 \times 10^{-6}$ ($p_K = 5{\cdot}80$), which is only about $\frac{1}{10}$ of that found by Bader ($1{\cdot}29 \times 10^{-5}$).

The preparation showed all the usual criteria of purity, however, and the solutions were made up with the usual precautions.

4-Nitroresorcinol.—4-Nitrosoresorcinol, prepared according to Henrich (*Ber.*, 1902, **35**, 4193), was oxidised with alkaline hydrogen peroxide (Borsche and Berkhout, *Annalen*, 1904, **330**, 106). In order to obtain any yield at all, it is essential (*a*) that the hydrogen peroxide should be not weaker than 3%, and (*b*) that the solution should be kept alkaline as long as possible, *i.e.*, after the reaction is over it must be kept boiling for at least ½ hour and concentrated to a convenient bulk, then acidified, and extracted with ether. The product after recrystallisation from hot water is the semi-hydrate, yellow crystals, m. p. 82°. It may be quickly dehydrated at 70° giving the anhydrous compound, m. p. 115°.

	First series.		Second series.		
v =	69	138	186	372	744
λ =	3·11	4·37	5·56	7·35	11·08
$K \times 10^6$ =	0·98	0·97	1·16	0·99	1·11

The mean value of K is $1{\cdot}04 \times 10^{-6}$ ($p_K = 5{\cdot}98$), which agrees fairly well with Bader's value, $1{\cdot}2 \times 10^{-6}$.

The compound is colourless in acid solution, and completely yellow between p_H 9 and 10. There is no further change in colour in more alkaline solution. The mean value of the first, and only, colorimetric constant is $K_1 = 1{\cdot}55 \times 10^{-9}$, $p_K = 8{\cdot}81$.

Discussion of Results.

It was not expected that the constants of compounds which undergo tautomeric changes would be as uniform as those of normal electrolytes; these changes are probably the cause of the "drifts" which were found in several cases. The irregularities which are found in some cases have been already traced to irreversible or only partly reversible changes brought about by the catalytic activity of the electrodes. The constant of the somewhat similar, although less sensitive, *p*-nitrophenol has been found by Holleman (*Rec.*

trav. chim., 1902, **21**, 432) to vary between 6·1 and 7·3 × 10^{-8}, while Hantzsch gives 9·6 × 10^{-8}. We have tested the constants over all available dilutions. In Table I the first dissociation constants are represented by K_e in order to distinguish them from the colorimetric constants—first, $_1K_c$; second, $_2K_c$, and third, $_3K_c$. The compounds have been arranged in each group as far as possible in the order of diminishing first dissociation constants, K_e. Some of these, however, can be regarded as practically identical, in view of the probable errors mentioned above. The mononitrodihydric, like the mononitromonohydric, phenols are about equal in strength, but the dinitro-compounds, like the dinitrophenols, show a considerable difference in this respect. It is, however, in the relation between K_e and the K_c values that both mono- and di-nitro-dihydric phenols show the greatest individuality: so much so that a single conductivity measurement, combined with a colorimetric determination in a solution of known p_H would serve to distinguish each compound quite clearly.

In Table I, the constants of the nitrophenols are given for comparison, the values of K_e being due to Holleman (*loc. cit.*) and those of K_c to Michaelis and Gyemant (*Biochem. Z.*, 1920, **109**, 166). The fourth, fifth, and sixth columns give the constants of the tautomeric changes into the yellow, then the red, and purple forms (if any). The figures in the third column assign each compound to its predominant tautomeric form (Ph. = phenolic; Qu. = quinonoid) and attempt to define its strength as an acid dissociating in this form (K_e').

The experimental constants summarise the equilibria between the tautomeric forms, HM_1 and HM_2, and the products of their dissociation. In the equations, HM_1 stands for the phenolic acid (Ph.), HO·R·NO_2, and HM_2 for the quinonoid or *aci*-form (Qu.), O:R:NO·OH:

$$K_e = \frac{[H^\cdot][M'_1 + M'_2]}{[HM_1 + HM_2]} \quad \text{and} \quad K_c = \frac{[H^\cdot][HM_2 + M'_2]}{[HM_1 + M'_1]} \ *$$

* K_e and K_c are the "apparent" constants, due to the two forms present together, and obtained by electrometric and colorimetric measurements, respectively. Experimental results show that these measurements do in many cases give "mass-action" or Ostwald constants, which do not vary more than those obtained in the case of some of those acids having no tautomeric forms. The expressions for K_e and K_c do not, however, imply constancy unless there are other constants regulating the equilibria between the tautomeric forms, as has been shown by Noyes (*J. Amer. Chem. Soc.*, 1910, **32**, 815; see also Prideaux, "Theory and Use of Indicators," p. 129, Constable, 1917). The drift in the case of some constants may be due to the fact that the equilibria between the tautomeric forms do not obey the law of "mass" or concentration action. We have not yet been able to devise a method of testing this hypothesis.

TABLE I.

Compound.	K_e, as p_K.	K_e', as p_K.	${}_1K_c$, as p_K.	${}_2K_c$, as p_K.	${}_3K_c$ as p_K.
Mononitrophenols.					
2-Nitrophenol	7·17	7·04 (Qu.)	6·05		
4- „	7·19		7·2		
3- „	8·0		8·35		
Dinitrophenols.					
2 : 6-Dinitrophenol	3·57		3·70		
2 : 4- „	4·0		4·06		
2 : 3- „	4·89				
2 : 5- „	5·16		5·16		
3 : 4- „	5·37				
3 : 5- „	6·68				
Dihydric mononitrophenols.					
3-Nitropyrocatechol	5·73	5·55 (Qu.)	4·95	11·03	High
2-Nitroresorcinol	5·80	5·80 (Qu.)	Low	6·34	—
4- „	5·98	5·98 (Ph.)	8·81	—	—
2-Nitroquinol	6·00	6·00 (Qu.)	3·25	7·2	10·2
4-Nitropyrocatechol	6·45	6·30 (Qu.)	5·56	10·96	—
Dihydric dinitrophenols.					
2 : 4-Dinitroresorcinol	3·05	3·3 (Ph.)*	3·9±0·4	—	—
3 : 5-Dinitropyrocatechol	3·54	3·14 (Qu.)	3·25	10·3	High
4 : 6-Dinitroresorcinol	3·98	4·60 (Ph.)	4·22	—	—
2 : 6-Dinitroquinol	4·00±0·2	3·3 (Qu.)†	2·8	5·2	9·05

* $a = 0{\cdot}4 \quad 0{\cdot}5 \quad 0{\cdot}7 \qquad p_{K_e}' = 3{\cdot}21 \quad 3{\cdot}24 \quad 3{\cdot}47.$

† $a = 0{\cdot}177 \quad 0{\cdot}211 \quad 0{\cdot}236 \quad 0{\cdot}280 \qquad p_{K_e}' = 2{\cdot}96 \quad 3{\cdot}13 \quad 3{\cdot}43 \quad 3{\cdot}64.$

Thus the constant K_c measures the tendency of the compound to undergo the tautomeric change under the influence of diminishing hydrogen-ion concentration, whether this change takes place in the undissociated molecule or in the ion. The constant K_e contains the molecules and ions which take part in the dissociation of the first hydrogen ion from both the tautomeric forms. Although neither of the two true dissociation constants can be deduced from K_e by a rigid algebraic proof, yet by taking into account numerical relations, on the assumption that the colorimetric constant gives correctly the relative amount of coloured form, $HM_2 + M'_2$, the true dissociation constants of HM_1 or HM_2 may be obtained. The following is an outline of the reasoning and calculations by which these true constants (column 3 in Table I) were derived.

Where K_e is much greater than K_c, it is practically identical with the true dissociation constant of the phenolic acid. On the other hand, where K_e is much less than K_c, it is practically identical with the true constant of the quinonoid acid. Where $K_e = K_c$, the original Ostwald theory of indicators must be used, since ionisation proceeds *pari passu* with tautomeric change. Where K_e and K_c are of the same order, but not too close to one another, the true constants may be calculated as described below. The

limiting ratios of K_e to K_c at which such calculations become necessary will depend on the accuracy with which the original constants are defined by the experimental work.

If $K_e \gtrless 100K_c$, K_e is the constant of the phenolic acid, for even at a degree of ionisation $\alpha = 0{\cdot}8$, the amount of the coloured tautomeride is negligible. In the case of the mononitro-compounds, the degree of ionisation does not exceed 0·05 at the highest dilutions investigated. In the case of the dinitro-compounds, we have not, in determining the constants, taken into account degrees of ionisation exceeding 0·5, since, according to the usual estimate, the secondary ionisation of a dibasic acid may begin to be appreciable at this degree of primary ionisation.

Even at much lower ratios of K_e/K_c, the true constant of the phenolic acid, K'_e, is not far from the observed constant, K_e. The correction of K_e to K'_e will be greatest if all the quinonoid tautomeride is present as ion, and we will make this assumption. The total ion concentration is $M'_1 + M'_2$ and this is equal to $M'_1 + x$, if x is the degree of transformation (of total compound) into M'_2. Suppose that the ratio K_e/K_c is 20, and that the conductivity is determined at a degree of dissociation of 0·25; then

$$(1 - x)/x = [H^+]/K_c \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which x is the degree of colour change, and

$$(1 - \alpha)/\alpha = [H^+]/K_e \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which α is the degree of ionisation.

Therefore, on the above assumption,

$$[H^+] = K_e(1 - \alpha)/\alpha = 3K_e \text{ and } x = 1/[1 + 3K_e/K_c) = 1/61$$

Also $$3(M'_1 + 1/61) = (1 - M'_1 - 1/61),$$

therefore $M'_1 = 0{\cdot}233$, and the true constant of HM_1, $K'_e = 0{\cdot}233[H^+]/0{\cdot}75$

or $$K_e' = 0{\cdot}93K_e; \text{ since } K_e = 0{\cdot}25[H^+]/0{\cdot}75.$$

Correction of the Constant of the Phenolic Acids.—When the ratio K_e/K_c is still lower, the observed constant may be corrected for the presence of the ion of the quinonoid form. From the conductivity results we select one or more values of α. Then $p_H = p_{K_e} + \log \alpha/(1 - \alpha)$. By introducing the corresponding value of $[H^+]$ into the equation $\log (1 - x)/x = p_{K_c} - p_H$, the value of x is obtained.

Now since $x = M'_2$, $M'_1 = \alpha - x$, and $HM_1 = 1 - \alpha$,

therefore $$p_{K'_e} = p_H - \log (\alpha - x) + \log (1 - \alpha) \quad . \quad . \quad (3)$$

Correction of the Constants of the Quinonoid Acids.—If K_c is greater than K_e, the observed electrolytic dissociation is mainly that of the

quinonoid form. The most natural assumption, and that which requires the largest correction of the observed constants, is that all the ion consists of M'_2, the remainder of the quinonoid form being present as HM_2. The true constant K'_e of this form can be determined by a simple calculation. Selecting a degree of transformation x (*e.g.*, 0·8), we calculate the corresponding value of $[H^+]$ from equation (1) above. Then substitute this in equation (2), and calculate α and hence also $x - \alpha$ from the equation $\log (1 - \alpha)/\alpha = p_{K_e} - p_H$.

Thus in the case of 3-nitropyrocatechol, when $x = 0{\cdot}8$, $p_H = 5{\cdot}55$, $\alpha = 0{\cdot}402$ at this p_H, and $x - \alpha = 0{\cdot}398$. Hence

$$p_{K'_e} = p_H + \log (x - \alpha)/\alpha = 5{\cdot}54 \quad . \quad . \quad . \quad (4)$$

In calculating α from equation (2) in cases where K_e shows a trend, that value of p_{K_e} is used which corresponds according to the conductivity results to *each* value of α. In these cases, the corrected constant also shows a trend.

Orientation and Polarity.—The orientation of the compounds tabulated can be regarded as exerting influence upon (1) the strengths of the phenolic acids, (2) the strengths of the quinonoid acids, and (3) the colorimetric constants of the tautomeric changes. The two principal aspects of orientation which have received most attention are (*a*) the propinquity of substituting groups, the well-known effects of which have long been systematised without any hypothesis as to mechanism; and (*b*) the alternation of substituting groups, the effect of which is intelligible on the electronic theory of valency.

It should be possible to explain the order of the constants which represent (1), (2), and (3) in a quantitative manner, by the principles (*a*) and (*b*). The residual charges, detected by Lewis's method in the electronic formulæ for $\cdot NO_2$ (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), cause it to act as a key radical in maintaining the polarity of a conjugated system. The nitrogen atom, on account of its mixed bond in $\cdot NO_2$ ($O{=}N{\dashrightarrow}O$), assumes a virtual positive charge and confers a virtual negative charge on the carbon atom to which it is attached, and this by alternation of the mean directions in which the electrons oscillate or vibrate, strengthens the virtual negative charges on the carbons in the 3- and 5-positions and weakens those in the 2-, 4-, and 6-positions.

Thus when a hydroxyl group is attached to the 3- or 5-position, weaker phenolic acids should result than when it is attached to the 2-, 4-, or 6-position. There might also be a reciprocal effect of the hydroxyl group on the nitro-group, which will become evident when the $\cdot OH$ becomes $:O$. Our results seem to show that the effect of

·NO·OH on :O, and reciprocally, is similar to that of $\cdot NO_2$ on ·OH; so that factors (*a*) and (*b*) act in the same sense on the quinonoid as on the phenolic acids. These effects may first be illustrated by the nitro- and dinitro-phenols.

o-Nitrophenol, in which factors (*a*) and (*b*) are both at a maximum, has a slightly higher constant than *p*-nitrophenol, in which (*b*) is favourable but (*a*) is less so (Holleman, *loc. cit.*). Both are higher in Table I than *m*-nitrophenol, in which (*b*) is unfavourable. The greater tendency to tautomeric change in the *o*- and *p*-compounds is shown by the dissociation of the ortho-compound largely as a quinonoid substance, and of the meta-compound in the phenolic direction. In the case of *p*-nitrophenol, dissociation and tautomeric change are almost parallel.

In the case of the dinitrophenols also, it is remarkable how close the colorimetric lies to the dissociation constant in those cases where both are known. The order of the constants agrees on the whole with the alternate polarity theory. In the strongest, 2 : 6-dinitrophenol, (*a*) and (*b*) are at a maximum; in the 2 : 4-compound (*b*) is favourable and (*a*) not so favourable. In 2 : 3-dinitrophenol, the strengthening effect of the 2-nitro-group is somewhat weakened by the opposing effect of the 3-nitro-group. In the 2 : 5-compound, the opposing effect of the second nitro-group is more marked as the hydroxyl group is exposed to it more directly. In the 3 : 4-, the nitro-group opposing the dissociation is nearer to the hydroxyl than that which favours it. In the 3 : 5-, both nitro-groups alternate incorrectly. It must be noted that the "opposition" of a nitro-group which alternates incorrectly is really only a smaller enhancing effect, since all dinitro-phenols are stronger acids than mononitro-phenols, owing, no doubt, to the more numerous chances for the formation of the quinonoid molecule *whatever* the position of the second nitro-group.

In contrast to the nitrophenols, the nitro-dihydric phenols show the most varied relations between first dissociation and colorimetric constants.

The Mononitro-compounds.—K_c is greater than K_e in the case of 2-nitroquinol, 2-nitroresorcinol, 3- and 4-nitropyrocatechols, 3 : 5-dinitropyrocatechol, and 2 : 6-dinitroquinol, which therefore dissociate chiefly or wholly as quinonoid acids; whilst K_e is greater than K_c in the case of 4-nitro-, and 2 : 4- and 4 : 6-dinitroresorcinol, which therefore dissociate chiefly or wholly as phenolic acids.

The first dissociation constants of the mononitro-compounds are of the order 1×10^{-6}, the constant thus being increased about 10-fold by the introduction of a second hydroxyl group into the molecule of *o*-nitrophenol. The nitro-group is in the ortho-position

to at least one hydroxyl group, *i.e.*, condition (*a*) is favourable, in all the compounds except 4-nitropyrocatechol, which has a distinctly lower constant than the others. One might perhaps expect 3-nitropyrocatechol to be a weaker acid than the 4-nitro-isomeride, instead of *vice versa*. The position of the second hydroxyl group appears, however, to have only a slight effect on the constant. Regarding the first four compounds in this series as derivatives of *o*-nitrophenol, we see that the effect of the second hydroxyl group in decreasing the constant $p_K = 7{\cdot}17$ (*i.e.*, increasing the constant K_c) of *o*-nitrophenol increases in the order 4 = 5, 3, 6. The order of increasingly favourable alternating effect (which agrees with the increase of constant in the order, *o*-, *m*-, and *p*-, in the case of mononitrophenols and some other compounds) is 4, 6, 5, 3. The order of increase in the case of the dihydroxybenzoic acids (with one hydroxyl group ortho to the carboxyl group) is 5, 4, 6, 3 (Lehfeldt, "Electrochemistry," Longmans), which is identical with the order required by condition (*a*) above, *i.e.*, mere propinquity without alternation. The dissociation of the carboxyl group would appear to be more powerfully affected by propinquity, (*a*), and that of the ·NO·OH group by alternation, (*b*), where the two principles are in opposition.

The Dinitro-compounds.—It was considered surprising by Bader (*loc. cit.*), in view of the negative character of hydroxyl, that dinitroquinol should be a weaker acid than 2 : 6-dinitrophenol. This may perhaps be explained as being due to a diminution of the negative polarity of the carbon attached to the ·NO·OH group by the opposing positive polarity of the carbon attached to the 4-hydroxyl group. 2 : 4-Dinitroresorcinol, in which the alternate polarities are in tune, is a stronger acid than 2 : 4- or even than 2 : 6-dinitrophenol.

Comparing the constants of the dinitro- with those of the corresponding mononitro-compounds, there is seen to be an increase in K (decrease in p_K of 1·5—3 units). The polarity of the second nitro-group always enhances that of the first, since the list examined includes only *m*-dinitro-compounds.

The order of the corrected constants is the same as that of the mononitro-compounds from which they are derived :

3-Nitropyrocatechol > 2-nitroresorcinol > 2-nitroquinol = 4-nitroresorcinol *
3 : 5-Dinitropyrocatechol > 2 : 4-dinitroresorcinol = 2 : 6-dinitroquinol > 4 : 6-dinitroresorcinol

* The meta-dinitro-derivative of 4-nitropyrocatechol has not been examined.

The tendency to undergo tautomeric change is measured by the colorimetric constants. The order of these is different from that

of the dissociation constants, and is nearly the same in the dinitro-compounds as in the mononitro-compounds from which they are derived. Thus it is apparently the orientation of one nitro-group in relation to the two hydroxyl groups which determines the number of tautomeric changes and the p_H at which they occur.

Order of $_1K_c$.

* 2-Nitroresorcinol > 2-nitroquinol > 3-nitropyrocatechol > 4-nitropyrocatechol > 4-nitroresorcinol,
2 : 6-Dinitroquinol > 3 : 5-dinitropyrocatechol > 2 : 4-dinitroresorcinol > 4 : 6-dinitroresorcinol †

* The constant is too high to be measured.
† The constant is rather uncertain.

To the second and third colorimetric constants given in our previous communication have now been added all those which can be determined. The nitroresorcinols do not give second constants, with the single exception of the 2-isomeride which undergoes its first change of colour at an exceptionally low p_H, whilst the change of the 4-isomeride occurs at an exceptionally high p_H. The second changes (half-way) to the red or brown forms occur at p_H's from 4 to 6 units lower than the changes (half-way) to the yellow form. The order of the second constants is very similar to that of the first:

$_1K_c$ | 2-N.R. > 2 : 6-N.Q. > 2-N.Q. = 3 : 5-N.C. > 2 : 4-N.R. > 3-N.C. > 4-N.C. > 4-N.R.
$_2K_c$ | 2 : 6-N.Q. > 2-N.R. > 2-N.Q. > 3 : 5-N.C. > 3-N.C. = 4N.C.

The only compounds which undergo the third change, to purple, are nitroquinols and nitropyrocatechols (but not 4-nitropyrocatechol); those in the latter class, however, only show this change in such strong alkali that p_{K_3} could not be determined. The order of the third constants is nearly the same as that of the second:

$_2K_c$ | 2 : 6-N.Q. > 2-N.Q. > 3 : 5-N.C. > 3-N.C. = 4-N.C.
$_3K_c$ | 2 : 6-N.Q. > 2-N.Q. > 3 : 5-N.C. > 3-N.C. —

UNIVERSITY COLLEGE,
NOTTINGHAM.

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CCCVIII.—*The Constitution of the Disaccharides. Part XV. Sucrose.*

By JOHN AVERY, WALTER NORMAN HAWORTH, and EDMUND LANGLEY HIRST.

THE normal variety of *d*-fructose has now been brought within the generalisation that hexoses and pentoses tend to exist ordinarily as amylene-oxide forms (Haworth and Hirst, J., 1926, 1858;

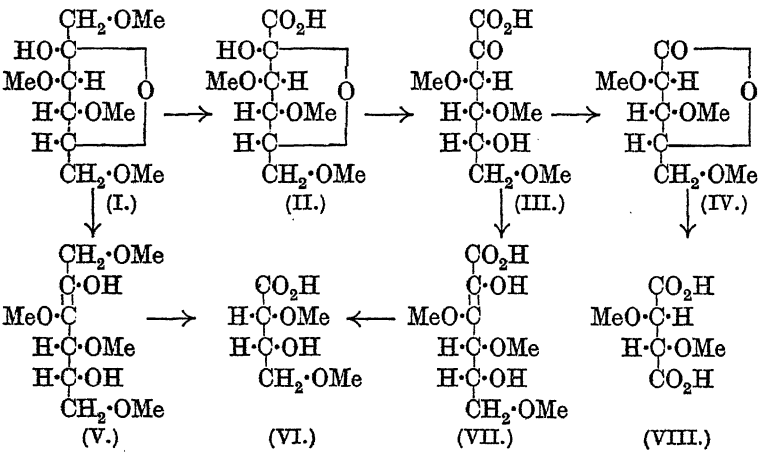
Haworth, Hirst, and Learner, this vol., p. 1040). This development has necessitated the abandonment of the butylene-oxide formula generally current for the normal sugar and latterly supported by the experiments of Irvine and Patterson (J., 1922, **121**, 2696), and has in consequence introduced many uncertainties into the reasoning by which the constitution of the more labile γ-isomeride of fructose was deduced. This consequence was indicated in the papers by two of us referred to above.

It will be seen on reference to the papers by Haworth and Linnell (J., 1923, **123**, 294) and by Haworth and Mitchell (*ibid.*, p. 301) that the inferences drawn from the experimental work therein recorded were based on the appropriation of the butylene-oxide structure for normal fructose. The consideration of a butylene-oxide structure for γ-fructose derivatives was for this reason excluded, the conclusion being drawn that "the choice of a constitution for the tetramethyl γ-fructose derived from methylated sucrose appears to be limited to one of the following forms: ethylene oxide, propylene oxide, amylene oxide." This later work on *n*-fructose has therefore rendered uncertain and insecure the arguments by means of which an amylene-oxide structure for tetramethyl γ-fructose has been deduced, and it was decided to take the present opportunity to review the whole position in the light of the experience gained in determining the constitution of other sugar derivatives. It has become evident in the meantime that, owing to the peculiar nature and extent of the isomerism in the sugar group, it is necessary to withhold the application of structural formulæ unless the substance under investigation has been transformed by well-defined methods into products which can be compared with or further degraded to give simple and crystalline reference compounds of definitely verified structure, such as the simple tartaric and hydroxyglutaric acids. In the earlier experiments (Haworth and Linnell, *loc. cit.*; Haworth and Mitchell, *loc. cit.*) the oxidative degradation products were, with few exceptions, liquid distillates and an extended examination of these substances has now yielded crystalline derivatives of such a nature that the structure of the tetramethyl γ-fructose from which they originated may be clearly deduced.

The experiments now to be described have involved a repetition of the work previously recorded on the oxidation of tetramethyl γ-fructose (I) by nitric acid and by alkaline permanganate, with the result that the accuracy of these experimental data has been substantiated, and proof has been obtained that in almost every case the products described, although liquids, were essentially homogeneous.

Oxidation of tetramethyl γ-fructose with either dilute or concen-

trated nitric acid leads, after esterification with ethyl alcohol, to the isolation of an ethyl ester giving C, 50·4; H, 7·8; OMe, 47·6, which agree reasonably well with either of the formulæ $C_{11}H_{20}O_7$ or $C_8H_{14}O_5$. This ethyl ester reduces Fehling's solution on warming, undergoes profound decomposition in the presence of hot alkali, and contains a reducing hydroxyl group which can be methylated to give a stable, non-reducing substance, the behaviour of which towards alkali is now normal. Owing to this behaviour with alkali, the quantitative hydrolysis of the ethyl ester gave figures which were higher than those calculated for $C_{11}H_{20}O_7$ and agreed with those required by a substance $C_8H_{14}O_5$; but, although the recorded analytical data and the behaviour during titration are in better agreement with the lactone formula $C_8H_{14}O_5$, originally proposed by Haworth and Linnell, yet this compound must now be recognised, for the following reasons, as the ethyl ester, $C_{11}H_{20}O_7$, of the lactol acid $C_9H_{16}O_7$ (II).



On methylation of this product, the higher homologue was obtained which was characterised by its conversion to a crystalline amide, m. p. 99—100°, identical with that previously described by Haworth, Hirst, and Nicholson (this vol., p. 1517). The relationship between the methyl ester obtained by these authors and the ethyl ester now described is thus demonstrated. The degradation of the lactol acid by means of alkaline permanganate yielded a hydroxymethoxy-acid which was isolated in the form of its methyl ester. In the experimental section the detailed analysis of this is described, and it is shown that the main product is occasionally accompanied by an impurity which substantially enhances the methoxyl and titration values. Specimens of the ester gave analytical figures which corresponded closely with those recorded by Haworth and Linnell

for their final esterified oxidation products, whilst others corresponded more nearly to methyl hydroxydimethoxybutyrate.* By treatment with methyl-alcoholic ammonia, each of them gave, in yield varying from 60—87%, the crystalline amide, m. p. 104—105°, of a hydroxydimethoxybutyric acid (VI), proof being thus afforded that the latter acid was the essential constituent. The same product was also obtained by direct oxidation of tetramethyl γ-fructose with alkaline permanganate (compare Haworth and Mitchell, *loc. cit.*), and the identity of the hydroxydimethoxybutyric acid from both these sources was demonstrated by the conversion of each specimen into the same crystalline amide. Methylation of the ester gave a methyl trimethoxybutyrate, which was characterised through the corresponding crystalline amide, m. p. 58—59°.

Under certain conditions, the above hydroxydimethoxybutyric acid appeared to lose the elements of water and give a hygroscopic anhydride, which has been described previously as a lactone by Irvine and Patterson (J., 1922, **121**, 2699) and by Haworth and Mitchell (*loc. cit.*). Sufficient evidence is not yet available, however, to enable a final choice to be made between the formulation of this anhydride as a lactone or a lactide (see footnote).

The application of the Weerman test (*Rec. trav. chim.*, 1917, **36**, 16) as a method for characterising α-hydroxy-acids by the action of sodium hypochlorite on their amides, indicated that the hydroxydimethoxybutyric acid under examination did not belong to this class, and the attempted oxidation of the free acid by means of nitric acid led to the recovery of the material unchanged, thus proving that the free hydroxyl group did not occupy a terminal γ-position in the chain. These indications pointed provisionally to the recognition of the hydroxydimethoxybutyric acid as a β-hydroxy-acid.

A complete verification of these results was secured, and a simple and direct proof of the structure of these substances and of γ-fructose derivatives was attained, by the degradative oxidation of the lactol acid $C_9H_{16}O_7$ (II) by means of barium permanganate in acid solution. Under conditions which required careful control, one

* The reason for this variability of composition becomes clear when it is recognised, as will appear later in this paper, that we were handling a β-hydroxy-acid. The parent substance of this product, β-hydroxybutyric acid, has been fully investigated by McKenzie (J., 1902, **81**, 1402), who has observed the readiness with which it passes into an anhydride form and into crotonic acid by loss of water. If in the present case a dimethoxycrotonic acid were formed, this would lead under the conditions employed to methoxymalonic acid, and ultimately to its methyl ester. We are at present studying the various forms of hydroxydimethoxybutyric acid, obtained synthetically from dimethoxyacetoacetic ester.

atomic proportion of oxygen was absorbed for each molecule of lactol acid, and a yield of nearly 50% of crystalline *d*-trimethyl γ-arabonolactone (IV) was obtained. We were able to recognise this compound with certainty, since we were in possession of the corresponding *l*-isomeride of the lactone (Baker and Haworth, J., 1925, **127**, 365; Haworth and Nicholson, J., 1926, 1899; Drew, Goodyear, and Haworth, this vol., p. 1244), and the properties of the two specimens are given for comparison :

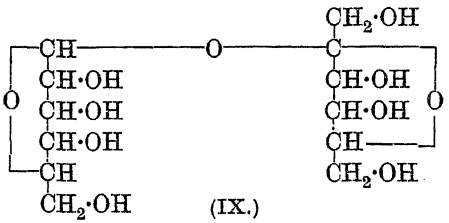
	d-Trimethyl γ-arabonolactone.	*l*-Trimethyl γ-arabonolactone.
M. p.	32—33°	33°
$[\alpha]_D$ (initial) in water.....	+44·5°	−44·2°
$[\alpha]_D$ (after 20 days)	+25·5°	−25·2°

We have confirmed the structure assigned to these lactones, wherein the methyl groups are allocated to the positions 2, 3, 5, by effecting their further oxidation with nitric acid. The *d*-trimethyl γ-arabonolactone originating from tetramethyl γ-fructose gave *l*-dimethoxysuccinic acid (VIII), identified as the crystalline methylamide and also as the amide, and these crystalline derivatives were compared directly with specimens which were specially prepared from *l*-tartaric acid (see later papers by Haworth, Hirst, and Learner and by Haworth and Jones).

The reaction between the lactol acid and acid permanganate is thus typical of the behaviour of either α-ketonic acids or ketol-acids which are potentially α-ketonic in nature (compare Ohle, *Ber.*, 1927, **60**, 1165), leading to the formation of a carboxylic acid containing one carbon atom less in the chain. Since the substance isolated in the present instance has been proved definitely to be 2 : 3 : 5-*d*-trimethyl arabonic acid, it follows immediately that the original lactol acid must have contained methyl groups in positions 3, 4, and 6. The oxide linking present in the lactol acid and also in tetramethyl γ-fructose must connect the carbon atoms in positions 2 and 5. Tetramethyl γ-fructose has therefore a γ- or butylene-oxide structure, and the lactol acid, $C_9H_{16}O_7$, is seen to have the constitution provisionally applied to it by Haworth and Hirst (1926). Similarly the hydroxydimethoxybutyric acid (VI) is recognised as 2 : 4-dimethyl *d*-erythronic acid.

The recent views we have expressed (Haworth, Hirst, and Nicholson, *loc. cit.*) relating to the structure of tetramethyl γ-fructose, resting on the analogy with other γ-sugars and on the ease of transformation of γ-fructose derivatives into furan bodies (see also Bergmann, J., 1923, **123**, 1277), are thus finally supported by the experimental results herein outlined. It follows that this sugar is now to be recognised as 1 : 3 : 4 : 6-tetramethyl fructose, and since

this derivative arises from the hydrolysis of methylated sucrose, the constitutional formula (IX), which we have applied in recent papers to sucrose, receives additional support and confirmation.



(IX.)

EXPERIMENTAL.

Oxidation of Tetramethyl γ-Fructose with Nitric Acid (d 1·42). *Isolation of the Ethyl Ester of the Lactol Acid* $C_9H_{16}O_7$ (II).—A mixture of tetramethyl γ-fructose (10 g.) and concentrated nitric acid (70 c.c.; *d* 1·42) was cautiously heated on the water-bath until at 70° a vigorous reaction ensued with evolution of nitrous fumes. The reaction was kept under control by cooling at intervals, and the temperature of the mixture was gradually raised to 93°. The reaction appeared to be complete after 1½ hours. Water was then added to the cooled solution and the nitric acid was almost entirely removed by distillation at 50—60°/13 mm., the usual precautions being observed to avoid undue heating during the concentration. This procedure was many times repeated and finally the product was taken down to a syrup. At this stage, absolute ethyl alcohol was added and distilled from the product to remove water. The syrupy residue was dissolved in 200 c.c. of absolute ethyl alcohol, containing 6 g. of hydrogen chloride, and boiled gently under reflux for 9 hours. Thereafter, the mineral acid was neutralised with silver carbonate, the solution filtered, and the solvent evaporated. The syrupy residue distilled without decomposition :

Fraction 1, at bath temperature up to 125°/0·1 mm.; 2·2 g., $n_D^{16°}$ 1·4500.

Fraction 2, at bath temperature 130—135°/0·1 mm.; 7 g., $n_D^{14°}$ 1·4520.

Fraction 3, at bath temperature 150°/0·1 mm.; 0·5 g., $n_D^{14°}$ 1·4564. Fraction 2, which showed $[\alpha]_D^{24°}$ + 25·8° in water (*c* = 2·7), gave the following analytical data—Found : C, 50·35; H, 7·75; OMe, 47·6. $C_{11}H_{20}O_7$ requires C, 50·0; H, 7·6; OMe, 47·0. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%. This material reduced Fehling's solution on warming and gave coloured decomposition products when heated with aqueous alkali. As stated on p. 2310, this product consisted essentially of the ethyl ester, $C_{11}H_{20}O_7$, of the

lactol acid, $C_9H_{16}O_7$ (II). *Titration.* 0·269 G. required 13·5 c.c. *N*/10-sodium hydroxide (on heating for ½ hour at 90°). Calc., for $C_{11}H_{20}O_7$: 10·2 c.c.; for the lactone, $C_8H_{14}O_5$: 14·2 c.c.

Methylation and Amide Formation.—A specimen of the above product (Fraction 2) was treated with Purdie's reagents for 5½ hours. A syrup which remained colourless when heated with aqueous alkali and which did not reduce Fehling's solution was obtained, distilling at 12 mm. from a bath heated at 155—160°. This showed $[\alpha]_D^{23°}$ + 3° in water (c = 1·07). *Titration.* 0·1048 G. required 4·2 c.c. *N*/10-sodium hydroxide for hydrolysis and neutralisation.

The methylated product was dissolved in methyl alcohol, saturated with dry ammonia, and cooled in ice, and the mixture was kept for 4 days. Removal of the solvent in a vacuum gave a crystalline product (yield above 60%), m. p. 99—100° (from light petroleum); $[\alpha]_{5461}^{21°}$ — 83° in water (c = 0·98). A specimen of the crystalline amide was mixed with the specimen of the amide $C_{10}H_{19}O_6N$, obtained by Haworth, Hirst, and Nicholson (this vol., p. 1517) from the corresponding methyl ester, and the m. p. showed no depression.

Oxidation with Alkaline Permanganate.—The product (2·5 g.) isolated from the process of oxidation with nitric acid as described above (Fraction 2) was treated at 70° with 2*N*-potassium hydroxide (20 c.c.) and with *N*-potassium permanganate (88 c.c.), the latter being gradually added with frequent shaking. In working up the product the alkali was neutralised with mineral acid in presence of ice, and after removal of the precipitated manganese oxides the filtrate was made slightly alkaline by means of potassium carbonate and evaporated (water-bath) to small bulk. Thereafter the whole of the water was removed in a high vacuum, yielding a white, solid mass. Preliminary experiments showed that no advantage was to be gained by extracting the solid with organic solvents. It was therefore dissolved in water and the organic acid liberated by acidifying with mineral acid. The water was then removed in a high vacuum, and the white mass extracted with chloroform. This extract yielded a syrupy organic acid which was esterified with methyl-alcoholic hydrogen chloride. The liquid ester distilled under 0·07 mm. from a bath heated to 100°, and showed $[\alpha]_D^{20°}$ + 19° (in water, c = 0·96) and $n_D^{17°}$ 1·4400; yield 0·8 g. (Found : C, 46·3; H, 7·9; OMe, 49·2. $C_7H_{14}O_5$ requires C, 47·2; H, 7·9; OMe, 52·2%). *Titration.* 0·0946 G. required 5·2 c.c. *N*/10-sodium hydroxide for hydrolysis and neutralisation (Calc. for $C_7H_{14}O_5$: 5·3 c.c.).

This product has been obtained on several occasions under similar experimental conditions to those outlined above, and the

physical properties and analyses of these specimens are tabulated below:

(*a*) $n_D^{17^\circ}$ 1·4400, $[\alpha]^{20^\circ}$ + 19°, C, 46·3; H, 7·9; OMe, 49·2%; (*b*) $n_D^{19^\circ}$ 1·4410, $[\alpha]_D^{19^\circ}$ + 22·4°, OMe, 54·9%; (*c*) $n_D^{13·5^\circ}$ 1·4390, OMe, 48·8%; (*d*) $[\alpha]_D^{20^\circ}$ + 21·8°, C, 46·75; H, 7·8; OMe, 61·2%; (*e*) n_D 1·4421, $[\alpha]_D$ + 31°, C, 47·8; H, 7·2; OMe, 60%.

The analyses of (*a*) and (*d*) were made independently by Fein-Chemie, G.m.b.H., Tübingen. These products correspond with that obtained by Haworth and Linnell (*loc. cit.*, p. 301), who quote C, 48·4; H, 7·2; OMe, 59·7%. It was evident that all these products were mixtures containing a variable quantity of a substance giving high methoxyl and titration values, and this factor is referred to in the footnote on p. 2311. That each of these specimens was essentially, however, methyl hydroxydimethoxybutyrate was demonstrated by treating them with methyl-alcoholic ammonia. This led to the isolation of the crystalline amide described below in yields from 60—87%, the largest yield being obtained from the specimen (*a*).

Hydroxydimethoxybutyramide was isolated as described above as crystals, m. p. 104—105° (from petroleum); $[\alpha]_{5461}^{19^\circ}$ + 37° in water (c = 1·05), and $[\alpha]_D^{19^\circ}$ + 33° [Found: C, 44·2; H, 8·0; N, 8·7; OMe, 36·2. $C_4H_7O_2N(OMe)_2$ requires C, 44·2; H, 8·0; N, 8·6; OMe, 38·0%].

Oxidation of Tetramethyl γ-Fructose with Alkaline Permanganate.—In general the method described by Haworth and Mitchell (J., 1923, **123**, 306) was followed, except that the product was isolated as the methyl ester as described in the earlier paragraph above. The ester distilled from a bath heated to 130° under 13 mm., and showed $n_D^{14^\circ}$ 1·4413. This material corresponded exactly with the specimens (*a*)—(*e*) described above, and gave on treatment with methyl-alcoholic ammonia a crystalline amide, m. p. 104—105°, identical in all respects with that described above as hydroxydimethoxybutyramide.

Hydrolysis.—A specimen of the above methyl ester was hydrolysed with dilute hydrochloric acid (5%) during 4½ hours at 80°. After the usual process of isolation, the product was distilled from a bath heated to 125° under 0·04 mm., and was obtained as a colourless, hygroscopic syrup having acid properties, but which did not crystallise on preserving in a vacuum over phosphoric oxide for several days. A further purification was effected by fractional distillation, and the substance remained as a colourless syrup. This appeared to be identical with the product obtained by Haworth and Mitchell (*loc. cit.*) and Irvine and Patterson (*loc. cit.*, p. 2699), and described as the lactone of hydroxydimethoxybutyric acid.

The observations now to be recorded indicate, however, that the product may have been a lactide of a β-hydroxy-acid.

Experiments on the Determination of the Structure of the Hydroxydimethoxybutyric Acid.—(a) *Weerman reaction on the amide.* Weerman's method (*loc. cit.*) for the characterisation of α-hydroxy-acids depends on the interaction of the amides of these acids with sodium hypochlorite, this reagent forming sodium *iso*cyanate with such amides but not with those of other hydroxy-acids. The qualitative test applied for the presence of sodium *iso*cyanate is the addition of hydrazine hydrate, followed by the addition of benzaldehyde, which leads to the isolation of benzalsemicarbazone. An alternative method is the addition of semicarbazide, which in presence of sodium *iso*cyanate forms crystalline hydrazidicarbonamide. When the test was applied to the hydroxydimethoxybutyramide which we had prepared during the present work, a negative result was obtained, indicating that this amide was other than an α-hydroxy-compound. Control experiments were carried out with gluconamide, trimethoxyglutaramide and acetamide, and only in the case of gluconamide was a positive result obtained, as should be the case.

(b) *Attempted oxidation with nitric acid.* The above result indicated that the related acid must be either a β- or a γ-hydroxy-acid. In the latter case the hydroxyl group would be in the terminal position as a $-CH_2\cdot OH$ group, which should be characterised by its ease of oxidation to a carboxyl group. When the substance was digested, however, with nitric acid (*d* 1·2) during 6 hours at 70—100°, it gave a product which, on conversion into the methyl ester, was identical with the original material, thus proving that no oxidation had taken place. This conclusion was verified by conversion of this ester into the crystalline hydroxydimethoxybutyramide, m. p. 104—105°. It became evident, on the basis of these results, that the hydroxydimethoxybutyric acid under examination was probably a β-hydroxy-acid.

(c) *Methylation of the ester.* The specimen (*a*) described previously, and consisting essentially of methyl hydroxydimethoxybutyrate, was methylated with Purdie's reagents, and the product on distillation showed $n_D^{12°}$ 1·4282; $[\alpha]_D^{21°}$ + 19° in water ($c = 1·04$). *Titration.* 0·1006 G. required 5·25 c.c. of *N*/10-sodium hydroxide for hydrolysis and neutralisation (Calc. for $C_8H_{16}O_5$: 5·24 c.c.). Found: C, 49·7; H, 6·5; OMe, 62·3. Calc.: C, 50·0; H, 8·3; OMe, 64·6%.

This product was identified as methyl trimethoxybutyrate by conversion into the crystalline amide. The trimethoxybutyramide separated from light petroleum as colourless needles, m. p. 58—59°,

$[\alpha]_D^{18°}$ + 40·5° in water (c = 1·09 (Found: C, 47·7; H, 8·5; N, 7·7; OMe, 49·7. Calc.: C, 47·5; H, 8·5; N, 7·9; OMe, 52·5%).

Confirmatory Proof of the Constitution of Tetramethyl γ-Fructose. Isolation of Crystalline d-2 : 3 : 5-*Trimethyl Arabonolactone by Degradative Oxidation of the Lactol Acid*, $C_9H_{16}O_7$.—The ethyl ester, $C_{11}H_{20}O_7$, of a lactol acid, $C_9H_{16}O_7$, was described as Fraction 2 on p. 2313. Preliminary experiments showed that the desired stage of oxidation by means of acidified permanganate was completed when one atomic proportion of oxygen had been absorbed. The details of the procedure are as follows: The material of Fraction 2 (3·2 g.) was hydrolysed during 3 hours at 90° with 60 c.c. of 2·5% hydrochloric acid. The solution was neutralised with silver carbonate, and the silver removed from the filtrate with the aid of hydrogen sulphide. The filtrate from the silver sulphide was evaporated, and the free lactol acid, $C_9H_{16}O_7$, was collected as a syrup, which was dissolved in 110 c.c. of water and mixed with 40 c.c. of *N*-sulphuric acid. Thereafter, a solution of barium permanganate (4%) was added very slowly until the required amount had been admitted, the reaction being conducted at room temperature. An excess of barium hydroxide solution was then added, followed by the admission of carbon dioxide to precipitate the excess of barium hydroxide. At this stage, the precipitated salts were removed by filtration, and to the solution, which contained the soluble barium salt of an organic acid, the equivalent of dilute sulphuric acid was added. The filtrate obtained after removal of barium sulphate was now evaporated under diminished pressure, and yielded a syrup which crystallised spontaneously when cold (yield 1 g.). The crystalline compound distilled under 11 mm. from a bath at 145°, and the distillate solidified instantly (yield 0·75 g.).

Extraction of this crystalline product with light petroleum left a minute quantity of residual oil which darkened in the air. From the solution in light petroleum, needles or shining plates crystallised according to the conditions of cooling (m. p. 32—33°; yield 0·6 g.); $[\alpha]_D$ + 44·5° in water (c = 0·712)—this initial value decreased during 18 days to the constant value + 25·5° (Found: C, 50·2; H, 7·7; OMe, 47·6. Calc. for $C_8H_{14}O_5$: C, 50·5; H, 7·4; OMe, 48·9%). *Titration.* 0·0512 G. required 2·7 c.c. *N*/10-sodium hydroxide for neutralisation, the substance behaving during titration as a lactone.

This product corresponds to *d*-trimethyl γ-arabonolactone, and in the theoretical section it is shown that the rotation values are equal and opposite to those of the *l*-isomeride, whilst the m. p. is identical.

A similar oxidation was carried out with the corresponding methyl

ester of the lactol acid, $C_{10}H_{18}O_7$ (compare Haworth, Hirst, and Nicholson, *loc. cit.*). In this example, the experiment was modified by omitting isolation of the free acid, inasmuch as control experiments indicated that the alcohol liberated on hydrolysis of the ester was not appreciably oxidised under the experimental conditions employed. The methyl ester (8·9 g.) was heated for 2½ hours at 85° with *N*/2-sulphuric acid (104 c.c.). Barium permanganate equivalent to one atomic proportion of oxygen was then admitted to the cold solution, which had been diluted to a volume of 500 c.c. by the addition of a further 100 c.c. of *N*/2-sulphuric acid and water. The product was isolated in the manner already described, and weighed 4·1 g., of which 3·0 g. were collected as a distillate under 11 mm. from a bath at 145°. This distillate crystallised immediately when cold. A similar portion of an oily by-product was again noticed. The recrystallised *d*-trimethyl γ-arabonolactone, m. p. 33°, weighed 2·6 g.

It should be added that qualitative tests conducted with the ethyl or methyl esters dissolved in acidified permanganate solution showed that the reaction proceeded slowly until hydrolysis of the ester had taken place. Oxidation then proceeded rapidly at room temperature. The oxidation proceeds smoothly and is accompanied by practically no change in the rotation value of the solution.

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THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCCIX.—*The Tautomerism of Amidines. Part VII. Methylation of Benzenyl-*p*-nitrodiphenylamidine.*

By CLIFFORD CHEW and FRANK LEE PYMAN.

THE alkylation by alkyl salts of open-chain amidines, in which one of the nitrogen atoms is attached to an aryl group and the other to a non-aryl (hydrogen or alkyl) group, yields as main products compounds alkylated on the arylamine nitrogen atom, together with small quantities of the isomeric alkyl derivatives. For example, benzenylphenylmethylamidine (I or II) gives with methyl iodide methylphenylamidobenzenylmethylimidine (III) in 62% yield, and dimethylamidobenzenylphenylimidine (IV) in 4% yield (Pyman, J., 1923, **123**, 367).

In previous papers (Pyman, J., 1923, **123**, 3359; Forsyth and Pyman, J., 1926, 2502) one of us has expressed the view that results

of this kind are due, not to the feebler basicity of the arylamino-group as compared with the alkylamino-group, as some previous

(I.) $CPh(:NPh)\cdot NHMe \rightleftharpoons CPh(:NMe)\cdot NHPh$ (II.)

(III.) $CPh(:NMe)\cdot NMePh$ $\qquad$ $CPh(:NPh)\cdot NMe_2$ (IV.)

investigators have supposed, but to the tendency of the aryl group to attract the double linking into the αβ-position. Thus, it was thought that benzenylphenylmethylamidine reacted in the form (I) to a much greater extent than in the form (II), owing to the influence of the phenyl group in the anilino-residue, and consequently gave (III) to a much greater extent than (IV), since the alkylation of open-chain amidines with alkyl salts leads to the attachment of the alkyl group to the nitrogen atom which is doubly linked to carbon (Pyman, J., 1923, **123**, 3359). Evidence that the structural effect is of greater importance than the relative basicities of the nitrogen atoms has been given in the papers quoted, and further evidence in favour of this view is afforded by the results of the present investigation.

Benzenyl-p-*nitrodiphenylamidine* (V or VI) gave on methylation with methyl iodide *benzenylmethylphenylamido*-p-*nitrophenylimidine* (VII) in 28·8% yield, and *benzenylmethyl*-p-*nitrophenylamidophenylimidine* (VIII) in 24·9% yield, together with 8·8% of unchanged material. Now, in benzenyl-*p*-nitrodiphenylamidine both nitrogen

(V.) $CPh(:NPh)\cdot NH\cdot C_6H_4\cdot NO_2 \rightleftharpoons CPh(:N\cdot C_6H_4\cdot NO_2)\cdot NHPh$ (VI.)

(VII.) $CPh(:N\cdot C_6H_4\cdot NO_2)\cdot NMePh$ $\qquad$ $CPh(:NPh)\cdot NMe\cdot C_6H_4\cdot NO_2$ (VIII.)

atoms are attached to phenyl groups, and the structural effect of the phenyl groups is thus balanced, but the two nitrogen atoms, which are present as anilino- and *p*-nitroanilino-residues respectively, differ considerably in basicity, for aniline has $K = 4{\cdot}6 \times 10^{-10}$ and *p*-nitroaniline $K = 1 \times 10^{-12}$. The results of the methylation thus show that the marked disparity between the yields of the two methyl derivatives, which is always observed when arylamine and alkylamine residues are in competition for a methyl group, has disappeared here on the elimination of the structural effect of a phenyl group attached to only one of the nitrogens, in spite of a considerable difference between the basicities of the two amino-residues. Further, it is noteworthy that the isomeride isolated in rather larger quantity is that in which the methyl group has become attached to the more basic nitrogen atom. This agrees with the results of alkylating open-chain amidines such

as benzenylmethylamidine, $NMe{:}CPh{\cdot}NH_2 \rightleftharpoons NHMe{\cdot}CPh{:}NH$, in which neither of the nitrogen atoms is attached to a phenyl group (Pyman, *loc. cit.*). The constitutions of the two methylated amidines (VII) and (VIII) were determined by synthesising them from the appropriate methylated amines, and in the course of this work various known methods for the preparation of amidines have been compared, and are referred to below.

EXPERIMENTAL.

Benzenyl-*p*-nitrodiphenylamidine was prepared by several of the available methods.

A. After Gerhardt (*Annalen*, 1858, **108**, 214). Benzanilide-iminochloride (53 g.) and *p*-nitroaniline (33 g.) in dry ether (1 l.) were kept for 4 days. The deposit (22 g.; m. p. 165—195°) was dissolved in hot alcohol (300 c.c.) and kept; the crystals (7·5 g.; m. p. 245—250°) which separated were dissolved in hot alcohol (150 c.c), and when the solution was basified with ammonia, the amidine separated (5·5 g.; m. p. 183°; yield 7%).

B. After Sen and Ray (J., 1926, 646). Benzanilide (10 g.), *p*-nitroaniline (7 g.), and phosphorus trichloride (170 g.) were heated under reflux for 4 hours in an oil-bath at 120—130°, and the amidine was isolated in 15% yield (2·38 g.; m. p. 180—182°).

C. After Hill and Rabinowitz (*J. Amer. Chem. Soc.*, 1926, **48**, 732). Benzanilide (10 g.), *p*-nitroaniline (7 g.), phosphorus trichloride (7 g.), and sodium-dried benzene (44 c.c.) were heated for 5 hours at 100°; the amidine was obtained in 8% yield (1·33 g.; m. p. 182°).

D. After Hill and Cox (*ibid.*, p. 3214). This proved to be by far the best method. To a well-cooled suspension of phosphorus pentachloride (11 g.) in sodium-dried benzene (50 c.c.), benzanilide (10 g.) was added, followed by *p*-nitroaniline (7 g.), and the mixture heated under reflux for 3 hours on the water-bath. The solvent was distilled off, the residue was well ground with aqueous ammonia, and the paste filtered. The precipitate was thoroughly extracted by grinding with cold alcohol and water, and the residue was crystallised from alcohol, the amidine being isolated in 61% yield (9·1 g. of m. p. 182—183° + 0·75 g. of m. p. 179—180°). In a repetition of this experiment with 40 g. of benzanilide, the amidine was isolated in 75% yield (48·7 g.; m. p. 182°).

Benzenyl-p-nitrodiphenylamidine (V or VI) crystallises from alcohol in long, lemon-yellow needles, m. p. 184° (corr.) (Found: C, 71·8; H, 5·1. $C_{19}H_{15}O_2N_3$ requires C, 71·9; H, 4·5%). It is insoluble in hot or cold water or in chloroform, but moderately soluble in hot alcohol or ether. On grinding the base with concentrated

hydrochloric acid, a colourless, crystalline *hydrochloride*, m. p. 261°, is obtained, from which the amidine can be regenerated by treatment with ammonia. This hydrochloride is very sparingly soluble in hot water, and when boiled with alcohol containing hydrochloric acid yields *p*-nitrobenzanilide (m. p. crude, 194°; purified, 199°; mixed with a known specimen of m. p. 200°, 200°). In an attempt to prepare a picrate from the amidine and picric acid in hot alcohol, *p*-nitrobenzanilide was again deposited.

Benzenylmethylphenylamido-p-*nitrophenylimidine* (VII).—*p*-Nitrobenzanilide-iminochloride (9 g.), which had been completely freed from hydrogen chloride by keeping in an evacuated desiccator over sodium hydroxide, and monomethylaniline (3·5 g.) in dry ethereal solution were kept over-night, and the solvent distilled. The residue was extracted with hot 2% hydrochloric acid (250 c.c.), which left crude *p*-nitrobenzanilide undissolved (7·2 g.; m. p. 190°; mixed m. p. with a known specimen, 195°). The extract deposited a further 0·26 g. of the same compound on cooling, and the filtrate from this was basified and extracted with ether. The ether residue (3·65 g.) was separated by means of light petroleum into monomethylaniline (1·18 g.; b. p. 193°) and crude amidine (2·3 g.; m. p. 120—128°; yield 19%). It is essential to free the iminochloride from hydrogen chloride before attempting the condensation with monomethylaniline, for otherwise the amidine is not formed. Consequently, it is not surprising to find that this amidine cannot be prepared by the method of Hill and Cox.

Benzenylmethylphenylamido-p-*nitrophenylimidine* crystallises from alcohol in pale yellow plates, which in thin layers have a silvery lustre, m. p. 138° (corr.) (Found: C, 72·5; H, 5·4; N, 12·8. $C_{20}H_{17}O_2N_3$ requires C, 72·5; H, 5·1; N, 12·6%). It is insoluble in hot or cold water, chloroform, or benzene, moderately soluble in cold alcohol, and readily soluble in ether or hot alcohol. The *picrate* separates from alcohol in yellow plates, m. p. 206° (corr.). It is almost insoluble in water or cold alcohol, and explodes when heated in a flame. The *hydrochloride* and *hydriodide* separated from water as gums which could not be crystallised.

Benzenylmethyl-p-*nitrophenylamidophenylimidine* (VIII) could not be isolated from the products of interaction of benzanilideiminochloride (free from hydrogen chloride) with *p*-nitromonomethylaniline in cold or hot dry ether, but was readily prepared by the method of Hill and Cox. Benzanilide (5 g.) was added to a well-cooled suspension of phosphorus pentachloride (5·5 g.) in sodium-dried benzene (25 c.c.). After thorough shaking, *p*-nitromonomethylaniline (3·8 g.) was added, and the mixture heated under reflux for 3 hours on a steam-bath. The solvent was distilled off, and the

residue extracted several times with hot water (1 l. in all), which left very crude benzanilide (0·85 g.; m. p. 140°) undissolved. On being cooled, the extract deposited a yellow product (2·25 g.; m. p. 140—170°) which gave on crystallisation from alcohol the amidine hydrochloride (0·75 g.; m. p. 218—220°), the mother-liquors containing *p*-nitromonomethylaniline. The filtrate from the yellow product was basified with ammonia and extracted with ether, which removed an orange syrup (5·25 g.). This was mixed with concentrated hydrochloric acid and a little alcohol, and filtered from more amidine hydrochloride (3·8 g.; m. p. 216—219°). A further small quantity of this was obtained from the filtrate, and all crops were combined and crystallised from alcohol, 2·78 g. of the pure salt being obtained (yield, 29%).

Benzenylmethyl-*p*-nitrophenylamidophenylimidine was obtained as a pale yellow syrup, which did not crystallise. It is insoluble in cold or hot water or in chloroform, but readily soluble in alcohol or ether. It yields well-crystallised salts. The *hydrochloride* crystallises from alcohol in colourless, rhombic prisms, containing 1EtOH which is not lost at 100°, and melts and effervesces at 226° (corr.) (Found: C, 64·0; H, 5·9. $C_{20}H_{17}O_2N_3,C_2H_6O,HCl$ requires C, 63·9; H, 5·8%). It is sparingly soluble in cold water, moderately soluble in cold alcohol, and very readily soluble in hot alcohol. The *hydriodide* crystallises from alcohol in pale yellow, anhydrous, rhombic prisms, m. p. 225° (corr.) (Found: C, 52·3; H, 4·5. $C_{20}H_{17}O_2N_3,HI$ requires C, 52·3; H, 3·9%). It is very sparingly soluble in cold water, alcohol, or acetone, but readily soluble in hot alcohol or acetone. The *picrate* crystallises from alcohol in yellow needles, m. p. 194° (corr.). It is sparingly soluble in hot water or cold alcohol, but readily soluble in hot alcohol.

*Methylation of Benzenyl-*p*-nitrodiphenylamidine by Methyl Iodide.*—Benzenyl-*p*-nitrodiphenylamidine (35 g.) and methyl iodide (35 c.c.) were heated under pressure for 3 hours at 100°. The partly crystalline product was mixed with acetone, and crude benzenylmethyl-*p*-nitrophenylamidophenylimidine hydriodide (13·8 g.; m. p. 220°) was collected. The filtrate was concentrated, basified with ammonia, and extracted with ether. The ether residue (27·3 g.) was crystallised from alcohol (220 c.c.), which deposited benzenylmethylphenylamido-*p*-nitrophenylimidine (10·2 g.; m. p. 136°) on keeping for 1 hour, whilst the filtrate deposited crude benzenyl-*p*-nitrodiphenylamidine (4·1 g.; m. p. 163°) on keeping over-night. The final mother-liquor was evaporated to a syrup and mixed with concentrated hydrochloric acid (10 c.c.) and a little acetone, whereupon benzenyl-*p*-nitrodiphenylamidine hydrochloride (0·43 g.; m. p. 249°) separated. The filtrate from this was deprived of acetone,

dissolved in dilute hydrochloric acid, and mixed with sodium iodide, crude benzenylmethyl-*p*-nitrophenylamidophenylimidine hydriodide (0·71 g.; m. p. 197°) being then deposited. The filtrate was basified and extracted with ether, which gave a semi-solid residue (10·3 g.). This was crystallised from alcohol and gave crude *p*-nitromonomethylaniline (0·82 g.; m. p. 150°), but no other crystalline material could be isolated from the filtrate. When the various crude products were purified by the methods described earlier in this paper, benzenylmethyl-*p*-nitrophenylamidophenylimidine hydriodide was obtained in 24·9% yield (11·36 g. of m. p. 225° + 0·76 g. of m. p. 224°), benzenylmethylphenylamido-*p*-nitrophenylimidine in 28·8% yield (9·71 g. of m. p. 138° + 0·37 g. of m. p. 137°), and benzenyl-*p*-nitrodiphenylamidine was recovered unchanged in 8·8% yield (2·67 g. of m. p. 181° + 0·41 g. of m. p. 178°).

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MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, August 9th*, 1927.]

CCCX.—*Low-temperature Oxidation at Charcoal Surfaces. Part IV. The Active Areas for Different Acids and their Relative Rates of Oxidation.*

By WINIFRED MARY WRIGHT.

IN previous communications (J., 1925, **127**, 1347; 1926, 1813, 3182), it was demonstrated that the surfaces of charcoals containing both iron and nitrogen could be differentiated by the method of selective poisoning into areas of different catalytic activities for the oxidation of oxalic acid. Whilst it was shown that these areas were differentiated in respect of their structure (the Fe–C–N, Fe–C, and C–C areas), of the rates of oxidation, and of the temperature coefficients of the oxidation processes on the areas, the method of estimating the total active carbon area from the amount of amyl alcohol absorbed only gave a maximum value for the fraction of the surface which was active. It is unlikely that the amyl alcohol is adsorbed preferentially only on the most active area if this is already covered with oxalic acid. It is also improbable that one amyl alcohol molecule is attached to but one carbon atom of the underlying surface. Since the active carbon area, even in very active promoted charcoals, greatly exceeds the more active areas

of the promoted iron and iron–nitrogen patches, it was suggested by Dr. E. K. Rideal that it might be possible to determine both the adsorption of the poison and the displacement of the acid effected on this area.

Two specimens of charcoal were employed, Merck's blood- and Kahlbaum's sugar-charcoal; each charcoal was powdered to pass an 80-mesh sieve and heated for 2 hours at a low red heat in silica crucibles before use. The amyl alcohol content of the aqueous oxalic acid–amyl alcohol solutions employed was determined by the drop-weight method, and the oxalic acid content by titration with permanganate as previously described. The results obtained are shown in Table I.

TABLE I.

A. Merck's Blood-charcoal.

Oxalic acid.			Amyl alcohol.		
Bulk concentration (g.-mol. per l.).	Adsorbed (g.-mol. per g. of C.).	Displaced (g.-mol. per g.).	Bulk concentration (g.-mol. per l.).	Adsorbed (g.-mol. per g. of C.).	Mols. of alcohol required to displace 1 mol. oxalic acid.
0·025	$6·93 \times 10^{-4}$	0	0	0	0
„	$5·76$ „	$1·17 \times 10^{-4}$	0·0156	$7·31 \times 10^{-4}$	6·3
„	$4·58$ „	$2·35$ „	0·0313	$14·35$ „	6·1
	$2·20$ „	$4·73$ „	0·0625	$26·5$ „	5·5
„	0·0 „	$6·93$ „	0·125	49·0	(7·1)
0·5	$42·0 \times 10^{-4}$	0	0	0	0
„	$38·3$ „	$3·7$ „	0·05	24·5	6·6
„	$34·0$ „	$8·0$ „	0·15	48·3	6·0
„	$30·1$ „	$11·9$ „	0·25		5·8
0·75	50·0 „	0	0	0	0
„	36·0 „	14·0 „	0·25	67·0 „	4·8
	B. Kahlbaum's Sugar-charcoal.*				
0·75	$36·9 \times 10^{-4}$	0	0	0	0
„	$33·9$ „	$3·0 \times 10^{-4}$	0·05	10×10^{-4}	3·3
„	$27·4$ „	$9·5$ „	0·15	26 „	2·7
„	$14·9$ „	$22·0$ „	0·25	40 „	1·8

* This was a hard brittle charcoal (unlike the soft charcoal used in Part I of this series).

It is clear from these data that the amyl alcohol is by no means preferentially adsorbed in the presence of oxalic acid, but that the number of mols. of amyl alcohol required to desorb one mol. of oxalic acid depends both on the relative concentrations of the two adsorbents and on the nature of the adsorbate. Since with blood-charcoal, at the concentration (0·025*M*) giving the maximum oxidation velocity, 6 mols. of the alcohol only displace 1 mol. of the acid, the adsorption of the former does not give a trustworthy means of estimating the active area.

A search for a more efficient poison was made. Saturated solutions of diphenyl ether, *tert.*-butyl *p*-aminobenzoate, allyl *p*-aminobenzoate, octadecyl acetate, and hexadecylcarbamide were tried, but none of these reduced the rate of oxidation of oxalic acid by more than 70%. Solutions of dibromoacetic acid, ethylene dibromide, saponin, and sodium palmitate were also used; of these the soap was most efficient, giving 75% poisoning, but owing to its colloidal nature it was unsuitable for estimating the active areas. Ethylene dibromide, though very slightly soluble, gave 50% poisoning. A saturated solution of ethylene dibromide in aqueous ethyl alcohol (4% alcohol) gave 93% poisoning with oxalic acid, but further addition of alcohol gave an increased oxygen-uptake, owing to some secondary effect. A few determinations of displacement of oxalic acid by this substance were made, and from the degree of poisoning the active areas were calculated, but these results are untrustworthy owing to the unknown effect of alcohol on the oxidation velocity.

An attempt was made to poison the charcoal for the oxidation of *M*-formic acid by the addition of salts. Silver nitrate, copper sulphate, and aluminium chloride in *N*/100- and *N*/10-solutions were tried, but none of these gave more than 15% poisoning.

Finally, a saturated solution of caproic acid (0·046*N*) was found to be a fairly effective poison of the charcoal for the acids investigated. Its absorption was determined by the drop-weight method.

The results of poisoning Kahlbaum's sugar-charcoal with caproic acid for the oxidation of four acids are given in Table II. [Contrary to our previous results (Part I, p. 1353), we find that formic acid is readily oxidised in the absence of impurities.]

Caproic acid is clearly a more selective poison than any material hitherto examined. We note that 2 mols. of both aminoacetic acid and formic acid, 1·5 mols. of malonic acid, and 1 mol. of oxalic acid are displaced on the adsorption of 1 mol. of caproic acid, from which we may deduce the relative areas of these molecules on adsorption. These small values are somewhat surprising, if, as is frequently assumed to be the case, caproic acid is adsorbed with its chain parallel or attached to the underlying carbon atoms. It appears that 1 mol. of caproic acid can displace only two carboxyl groups (compare formic, aminoacetic, and oxalic acids). In every case, complete poisoning would be obtained when $3{\cdot}1 \times 10^{-4}$ g.-mol. (mean value of *A*) of caproic acid is adsorbed per g. of charcoal.

The total carbon area active for oxidation is thus identical for all the four acids investigated on this particular charcoal, whilst the rates of oxidation of the various acids at their respective maxima

TABLE II.

Acid.	M.	$X \times 10^4$.	k.	P.	$d \times 10^4$.	$a \times 10^4$.	d/a.	$D \times 10^4$.	$A \times 10^4$.
Oxalic	0·015	4·5	0·75	62	2·1	2·0	1·05	3·4	3·2
„	„	„	„	91	3·2	3·1	1·03	3·5	3·4
Formic	0·5	6·2	0·55	11	0·6	0·4	1·5	5·4	3·6
„	„	„	„	69	4·1	2·05	2·0	6·0	2·9
Malonic	0·05	7·6	0·43	48	2·1	1·3	1·6	4·4	2·7
„	„	„	„	70	3·2	2·0	1·6	4·6	2·9
Aminoacetic	0·50	6·8	0·22	37	2·1	1·1	1·9	5·9	3·0
„	„	„	„	88	5·4	2·6	2·1	6·1	3·0
Oxalic *	0·015	4·5	0·75	95	1·33			1·4	
Formic * ...	0·5	6·2	0·55	93	3·0			3·25	

M = Concentration for maximum rate of oxidation (g.-mol. per litre).
X = Acid adsorbed on unpoisoned charcoal (g.-mol. per g. of charcoal).
k = Reaction velocity on „ „ (c.c. O_2 per g. of C per hr.).
P = % Poisoning.
d = Acid displaced for P % poisoning (g.-mols. per g. of C).
a = Caproic acid adsorbed for P % poisoning (g.-mols. per g. of C).
D = Acid displaced for complete poisoning (g.-mols. per g. of C).
A = Caproic adsorbed „ „ „ („ „ „).

(D and A are calculated on the assumption that the degree of poisoning is proportional to the amount of acid displaced, or of poison adsorbed, although the results show that this is not strictly accurate.)

* These were poisoned with saturated ethylene dibromide in 4% aqueous alcohol. Malonic and aminoacetic acids were not poisoned readily by this substance.

are by no means identical. We may attempt a revaluation of the active area per g. of charcoal from these data. The total specific area of the charcoal, as determined by the saturation point of methylene-blue (see Part I), is 185 sq. m. per g. Since there is some doubt as to whether the methylene-blue method actually gives the total area, owing to the inability of the large molecules of the dyestuff to penetrate into the micropores of the charcoal, the surface saturation point of oxalic acid was determined from the adsorption isotherm.

From Table I, it is noted that 37×10^{-4} g.-mol. is adsorbed per g. from a 0·75M-solution; the adsorption isotherm is inconveniently flat near the maximum, but we may assume the maximum to be at *ca.* 40×10^{-4} g.-mol. per g.

The area of the adsorbed oxalic acid molecule is unknown, but, regarding it as equal to that of two expanded carboxyl groups, we obtain 50 Å. per mol., giving an area of 1212 sq. m. per g., or some seven times greater than that given by the methylene-blue method. The amount of oxalic acid displaced on complete poisoning by caproic acid is $3{\cdot}5 \times 10^{-4}$ g.-mol. per g., or 8·75% of the total

surface is effective; on poisoning with ethylene dibromide, $1{\cdot}4 \times 10^{-4}$ g.-mol. per g. is displaced, or 3·5% of the total surface is effective, when the oxalic acid is employed as a means of evaluating the total area. These values are considerably smaller than those given previously where methylene-blue was employed. They are probably more accurate, in that the amount of poison adsorbed agrees closely with the amount of acid displaced, the poison being very much more preferential in its action than amyl alcohol.

Experiments with Promoted Charcoal.—An active promoted charcoal was prepared from sugar, carbamide, and ferric chloride, and the rates of oxidation of the four acids were determined on specimens of this charcoal. The oxidations due to the presence of the Fe–C–N and Fe–C areas were determined in the manner previously described by poisoning with solutions of potassium thiocyanate and potassium cyanide. The relative rates of oxidation of the four acids on the unpoisoned promoted charcoal are:

Acid.	C.c. of O_2 per g. per hr.	Relative rate.	Relative rate on sugar-charcoal.
Aminoacetic	1·2	1	1
Malonic	0·74	0·6	2
Formic	4·4	3·6	2·5
Oxalic	5·3	4·4	3·4

It will be noted that malonic acid is oxidised relatively slowly on the promoted charcoal. It was found also that there was no appreciable alteration in its rate of oxidation on the addition of either potassium cyanide or potassium thiocyanate, an indication that the promoted areas in the charcoal are not effective in oxidising this acid. The final product of oxidation of malonic acid (see Part I) is glyoxylic acid, and it is probable that hydroxymalonic acid is formed as an intermediate oxidation product. This hydroxy-acid may poison the iron in the presence of oxygen by the formation of a complex similar to that formed by ferrous salts with hydrogen peroxide in Fenton's test for hydroxy-acids. The transient purple of this test can indeed be obtained on application of Fenton's reagents to a solution of malonic acid which has been agitated with charcoal in the air for some hours. The two breaks in the velocity–poisoning curves indicative of the presence of two promoted areas (compare Pt. III) could be obtained with both aminoacetic and formic acids, and show that these acids, like oxalic acid, oxidise at different speeds on the three types of surface (the Fe–C–N, Fe–C, and C–C areas) present in the charcoal.

It was found difficult to obtain accurate values for the effective areas of these promoted areas for formic and aminoacetic acids, since the iron is slowly extracted from the charcoal in the presence

of these acids. The approximate values are given in the following table :

Acid.	Velocity (c.c. of O_2 per g. per hr.) on Fe–C–N area.	Fe–C area.
Aminoacetic	1·08	0·009
Formic	3·90	0·042
Oxalic	4·37	0·049

The relative areas were found to be 9·1 sq. m. per g. for the Fe–C area and 5·5 sq. m. per g. for the Fe–C–N area. It will be noted that the relative rates of oxidation for the acids on the promoted Fe–C–N area are not widely different from those on the sugar-charcoal, and although the experimental error is much greater on account of the small velocities observed, a similar sequence in velocities is noted on the Fe–C area. We may conclude that the active patches on such charcoals are definite in extent and possess the property of oxidising a number of different acids, and that the difference in speed of reaction for different acids is to be attributed to the ease of reaction of the acid with the excited oxygen. This is probably present on the surface of the charcoal in the form of a peroxide which may be desorbed from the surface by excess of acid.

That the ease of oxidation of these fatty acids in aqueous solution follows the same sequence as the reaction velocity of catalytic oxidation at charcoal surfaces was demonstrated by measuring the depolarising capacity of solutions of these acids. These were determined by electrolysis between a small platinum cathode and a large, smooth platinum anode of an $N/5$-solution of sulphuric acid which was also N with respect to the acid under investigation. With the aid of a normal calomel electrode, salt junction, and Wheatstone bridge, the anode potential could be determined for various current densities at 25°. The curves obtained for the various acids are depicted in the figure.

It will be seen that neither acetic nor succinic acid exerts any appreciable depolarising action on the anodic evolution of oxygen, and neither of these acids is oxidised at observable rates with the charcoals hitherto examined by us ; on the other hand, the depolarising powers of oxalic, formic, and aminoacetic acids fall in the order of their rates of oxidation on charcoal surfaces. Tyrosine, a substance readily oxidised at charcoal surfaces, is included for comparison.

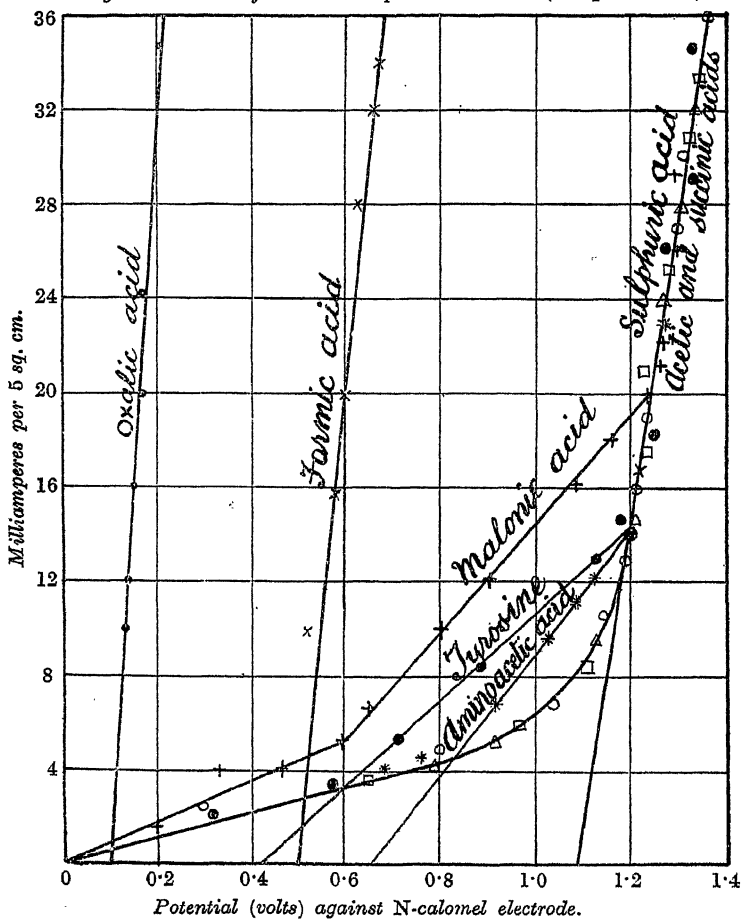
Summary.

The oxidation rates and the effects of poisoning with caproic acid on charcoal surfaces have been examined for formic, oxalic, malonic, and aminoacetic acids. It is found that the amounts

of poison absorbed required to inhibit the oxidation of these acids are identical. The effective catalytic area is found by this method to be about 4—8% of the total surface. With the exception of

FIG. 1.

Electrolytic oxidation of acids on a platinum anode (21 *sq. cm. area*).



$N/5$-H_2SO_4 ○. $N/5$-H_2SO_4 + N acetic acid □. $N/5$-H_2SO_4 + N-succinic acid △. $N/5$-H_2SO_4 + N-aminoacetic acid ∗. $N/5$-H_2SO_4 + $N/10$-tyrosine ●. $N/5$-H_2SO_4 + N-malonic acid +. $N/5$-H_2SO_4 + N-formic acid ×. $N/5$-H_2SO_4 + N-oxalic acid ●.

malonic acid, all these acids oxidise more rapidly on the promoted Fe–C–N and Fe–C areas than on pure charcoal. The poisoning of the promoted charcoal in the case of malonic acid is attributed to the hydroxy-acid formed as an intermediate oxidation product.

The velocities of oxidation at their respective maximum rates are shown to follow the order of depolarisation for oxygen liberated at a platinum electrode.

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CCCXI.—*Orientation Effects in the Diphenyl Series. Part IV. The Reduction of Bandrowski's and of Strakosch's Dinitrobenzidines, and the Condensation of the Products with Benzil. The Nitration of 2-Nitrodiacetylbenzidine and of 4:4′-Dibromodiphenyl.*

By RAYMOND JAMES WOOD LE FÈVRE, DANIEL DONALD MOIR, and EUSTACE EBENEZER TURNER.

IT was recently shown (Le Fèvre and Turner, J., 1926, 1759) that Cain's supposed 3:3′-dinitrobenzidine (Bandrowski's dinitrobenzidine) was the 2:3′-derivative, but, as was then fully realised, one difficulty still remained in connexion with the supposed identity of the two quinoxalines obtained by Cain and later by Brady and McHugh (J., 1923, **123**, 2047) by condensation with benzil of the tetra-amines derived from Bandrowski's and Strakosch's dinitrobenzidines. In view of the difficulty of purifying Bandrowski's compound (compare Le Fèvre and Turner, *loc. cit.*), an obvious explanation of the above facts was that the quinoxaline obtained from the Bandrowski material actually was derived from the Strakosch product, present as an impurity in the specimens of Bandrowski's dinitrobenzidine used for reduction.

We hesitated to advance this as a solution of the problem in the light of the conclusions of Brady and McHugh, but, in view of the fact that the Bandrowski's dinitrobenzidine prepared by Le Fèvre and Turner (*loc. cit.*) had m. p. 236—237°, *i.e.*, higher than that given by previous workers, we have carefully re-investigated the compounds concerned. We find that, in spite of the difficulties mentioned above, Bandrowski's dinitrobenzidine, *melting at* 233°, does, on reduction, followed by treatment with benzil in glacial acetic acid, give, as the most readily isolable product, a quinoxaline which is undoubtedly identical with that derived normally from 3:3′:4:4′-tetra-aminodiphenyl, and that therefore the initial Bandrowski's dinitrobenzidine must have contained some 3:3′-dinitrobenzidine.

There is a very marked difference in the behaviour of the two

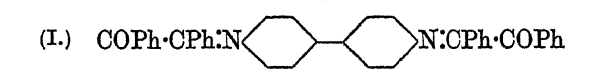
tetra-amines when treated with benzil. With that derived from Strakosch's dinitrobenzidine, a copious precipitate is obtained, but with that derived from Bandrowski's dinitrobenzidine (m. p. 233°, or a little lower), only a *small quantity* of precipitate results. The smallness of the yield was not mentioned by previous authors, and the foregoing explanation was therefore not suspected. The amount of Strakosch's dinitrobenzidine necessary to depress the m. p. of pure Bandrowski's dinitrobenzidine from 236—237° to 233° has been estimated, by examining artificial mixtures, as 2—3%. Such a proportion is in approximate agreement with the yields of quinoxaline obtained from various samples (see Experimental).

During the progress of this work, Hodgson (J., 1926, 2384) showed that some 3 : 3′-dinitrobenzidine was *formed* during the nitration of diphthalylbenzidine, but he did not attempt to demonstrate the presence of the 3 : 3′-isomeride in what has always been called Bandrowski's dinitrobenzidine, *i.e.*, a compound melting in the neighbourhood of 233°.

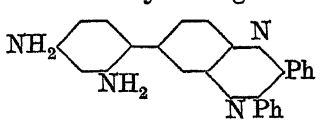
Methods previously described (Brunner and Witt, *Ber.*, 1887, **20**, 1024; Brady and McHugh, *loc. cit.*) for the reduction of Bandrowski's dinitrobenzidine proved unsatisfactory, but it was readily effected by iron powder, water, and ferric chloride.

Brady and McHugh showed that the two tetra-amines behaved very differently towards nitrous acid. A marked contrast was also observed when each was warmed in dilute acetic acid solution with acetic anhydride. In one case (2 : 3′ : 4 : 4′), bunches of white needles slowly separated from a purple solution, whilst in the other case there was immediate formation of an iridescent cream-coloured paste of minute needles. The compounds formed were the expected *tetra-acetyl* derivatives.

It was shown (Le Fèvre and Turner, J., 1926, 2476) that Cain's benzidine–benzil condensation product was dibenzoylbenzylidenebenzidine (I). 2 : 3′ : 4 : 4′-Tetra-aminodiphenyl (Bandrowski's tetra-amine) would therefore be expected to condense rapidly with

(I.) 

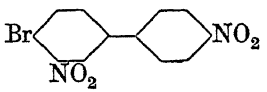
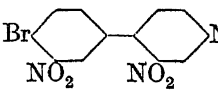
benzil in cold glacial acetic acid solution to give (II), which should condense further with benzil only at higher temperatures. We

(II.) 

find that (II) is soluble in cold acetic acid, and that on heating the solution in which it is formed it undergoes further condensation

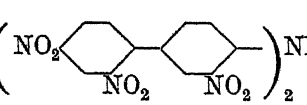
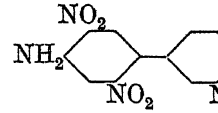
with production of what is evidently a mixture of the two benzoylbenzylidene derivatives and the dibenzoylbenzylidene derivative corresponding with (I).

Although we have improved upon the usual process for obtaining Bandrowski's dinitrobenzidine, we attempted to prepare the corresponding tetra-amine without recourse to the parent dinitrobenzidine. 4-Bromo-4′-nitrodiphenyl was nitrated to give 4-*bromo*-3 : 4′-*dinitrodiphenyl* (III) which on further nitration gave 4-bromo-2′ : 3 : 4′-trinitrodiphenyl (IV) (Le Fèvre and Turner, J., 1926, 2041). Small quantities of the latter compound were readily convertible into 2′ : 3 : 4′-*trinitro*-4-*aminodiphenyl*, but the large-scale conversion proved unsatisfactory. The reduction of the trinitroamine was accordingly not fully investigated.

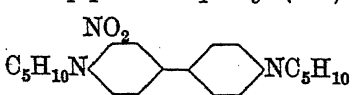
(III.)   (IV.)

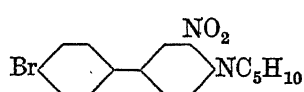
When (IV) was dissolved in boiling nitrobenzene, and dry ammonia was passed through, a bright yellow substance was obtained, apparently 4 : 4′-*bis*-op-*dinitrophenyl*-2 : 2′-*dinitrodiphenylamine* (V). The results of similarly treating other compounds containing reactive halogen atoms are recorded in the experimental part.

When attempting to prepare 2 : 3′-dinitrobenzidine from 2-nitrodiacetylbenzidine (Le Fèvre and Turner, *loc. cit.*), we observed that an impure product occasionally results, apparently owing to overnitration. We have now obtained from such products, by application of the method used for preparing Bandrowski's dinitrobenzidine from diphthalylbenzidine, the sparingly soluble *sulphate* of 2 : 5 : 3′-*trinitrobenzidine* (VI), the constitution of which is proved

(V.)   (VI.)

by its conversion by the perbromide method into 4 : 4′-*dibromo*-2 : 5 : 3′-*trinitrodiphenyl*, this in turn being identified by its ready conversion into a *di*piperidino-compound, *viz.*, 2 : 5 : 3′-*trinitro*-4 : 4′-*dipiperidinodiphenyl* (VII).


(VII.)

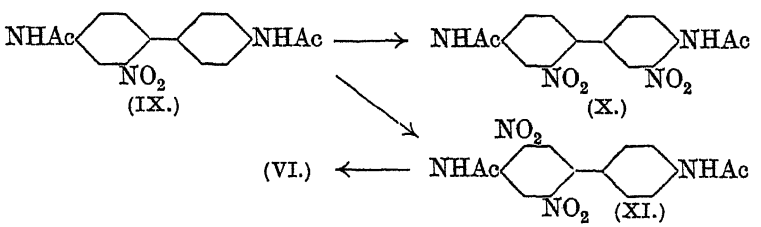

(VIII.)

Lellmann (*Ber.*, 1882, **15**, 2838) had previously isolated by overnitration of dibromodiphenyl a trinitro-derivative, having a m. p.

some 70° lower than that of the above compound. Lellmann's compound is, however, the isomeric 4 : 4′-*dibromo*-2 : 3′ : 5′-*trinitrodiphenyl* (XIV), since 4-*bromo*-2 : 3′ : 5′-*trinitro*-4′-*piperidinodiphenyl* (VIII) is formed from it with great readiness.

Comparison of the results now obtained with those previously recorded (this series) appears to show that, amongst the examples studied, the *op*- directive influence of groups decreases in the order NHAc > *p*-NHAc·C_6H_4 > *p*-Br·C_6H_4 > Br, the first being very powerful. In the light of this, it is possible to discuss the complete nitration of 2-nitrodiacetylbenzidine (IX) and of 4 : 4′-dibromo-2-nitrodiphenyl.

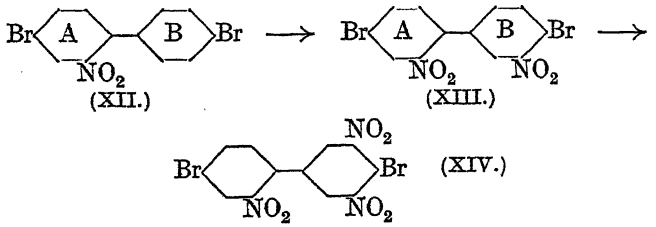
The former is now known to give as the main product 2 : 3′-dinitrodiacetylbenzidine (X), but since it has been shown (Bell and Kenyon, J., 1926, 2705) that 4-acetamidodiphenyl nitrates in position 3, *i.e.*, in the nucleus containing the acetamido-group, it would not be surprising, particularly in view of the now established powerful directive effect of this group, if some of the isomeric 2 : 5-compound (XI) were also formed. Further nitration of a



mixture of (X) and (XI) would only be expected to affect (XI). We have actually found that (X) is unaffected by fuming nitric acid at 25°, *i.e.*, under conditions more drastic than those under which the trinitro-compound (VI) was originally formed. The nitration of 2-nitrodiacetylbenzidine, therefore, in all probability proceeds in accordance with the scheme outlined above.

The nitration of 4 : 4′-dibromo-2-nitrodiphenyl has previously been shown (Dennett and Turner, J., 1926, 476) to be controlled entirely by the bromine atom in the ring B (XII), since nucleus A is rendered ineffective owing to the presence of the nitro-group : 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl is therefore quantitatively produced. In the further nitration of this compound, each nucleus will be as ineffective upon the other as was A in (XII); that is, entry of the third nitro-group will be controlled only by the nitro-group and bromine atom present in the nucleus attacked. In nucleus B (XIII) these groups will both favour nitration in position 5, whilst in A (XIII) they have antagonistic influences. Nitration

therefore occurs in B, with formation of the above 4 : 4′-dibromo-2 : 3′ : 5′-trinitrodiphenyl (XIV).



EXPERIMENTAL.

Preparation of 2 : 3′-Dinitrobenzidine.—The following modification of the usual process is more satisfactory, particularly as regards yield: Powdered diphthalylbenzidine (270 g.) was slowly dissolved in 1800 c.c. of fuming nitric acid (*d* 1·5), the temperature not being allowed to rise above 10°. After 15 minutes, the mixture was poured on 5 kg. of crushed ice, the resulting light yellow precipitate being washed first with boiling water and then with hot methylated spirit (yield, 350 g.).

For hydrolysis, 270 g. of the above product, previously dried at 100°, were dissolved in 1200 c.c. of concentrated sulphuric acid, and the solution was heated at 135—140° for 20 minutes. After being cooled, the acid solution was poured into 5 l. of water, the temperature not being controlled. The precipitate first formed redissolved as the temperature rose, and the nearly clear solution, after filtration, deposited long, yellow-brown needles when cooled. These were collected and crystallised from dilute sulphuric acid (1 : 4 by vol.). The crystals so obtained were ground with aqueous ammonia, and the red base (m. p. 225°) was filtered off. One crystallisation from phenol–alcohol gave a definitely crystalline specimen, m. p. 233°. Two further crystallisations raised the m. p. to 234—235°, and to 236—237° (uncorr.), respectively, the final product being pure 2 : 3′-dinitrobenzidine.

Melting Points of Mixtures of 2 : 3′- and 3 : 3′-Dinitrobenzidines.—The specimens of the two bases used had m. p. 243—244° and 281—282° (corr.) respectively. A mixture containing 90% of 2 : 3′-base and 10% of 3 : 3′-base shrank at about 224°, showed definite signs of melting at 233°, and ran to a liquid at 237°; one containing 94·8% of 2 : 3′- and 5·2% of 3 : 3′ base reached the same three stages respectively at 226°, 236°, and 238·6°; and the 97·6–2·4% mixture at 238°, 239·9°, and 241·4°. The above figures were obtained by the use of a completely immersed, short-stem standard thermometer. The corresponding uncorrected figures,

taken simultaneously with an ordinary thermometer, were: 218°, 227°, 231°; 220—221°, 229°, 232°; and 232°, 233°, 235°, respectively.

Reduction of Bandrowski's Dinitrobenzidine.—Preliminary experiments showed (1) that the tetra-amine is readily soluble in water, and (2) that the solution rapidly oxidises in the air. The following procedure was therefore adopted: 100 G. of iron powder were thoroughly wetted with 100 c.c. of water at 100°; 10 g. of 2 : 3′-dinitrobenzidine were then added, and the whole was well mixed. On the addition of a little ferric chloride, reduction proceeded vigorously, and was completed by ½ hour's heating with continuous stirring. Water was added, and the tetra-amine obtained in clear aqueous solution by filtration. Evaporation of this in a current of carbon dioxide (*a*) gave 2 : 3′ : 4 : 4′-tetra-aminodiphenyl as a purplish solid.

Reduction of Strakosch's Dinitrobenzidine.—10 G. of the dinitrobenzidine were shaken in a litre flask with 150 c.c. of methylated spirit until in fine suspension. 200 C.c. of water were added, followed by 70 g. of sodium hyposulphite, and the mixture was heated on the boiling water-bath for an hour. During this time, the colour changed from red to pale grey, and the suspended solid almost completely dissolved. The alcohol was then distilled off, the residue extracted with a mixture of water (150 c.c.) and concentrated hydrochloric acid (150 c.c.), the extract filtered, and the filtrate evaporated to about 2/3 of its original bulk. On cooling, pale brown needles of 3 : 3′ : 4 : 4′-tetra-aminodiphenyl hydrochloride separated. These, after being crystallised from dilute hydrochloric acid, were ground with aqueous ammonia; the liberated base crystallised from a mixture of phenol and alcohol in greyish plates, m. p. about 172—173° (Found: N, 26·5, 26·3. Calc.: N, 26·2%).

Condensation of 2 : 3′ : 4 : 4′*-Tetra-aminodiphenyl with Benzil.*—(a) *In the cold.* The flask in which the evaporation and extraction (*a* above) had been effected was tared, after its contents had been dried, and the soluble material was extracted four times with 10 c.c. of warm glacial acetic acid. Filtration from a considerable quantity of dark-coloured insoluble material enabled the amount of tetra-amine in solution to be calculated (generally of the order of 2 g.). A solution of the required quantity of benzil in cold glacial acetic acid was added to the cooled filtrate. After some minutes, crystallisation could be induced by scratching, but even after 12 hours the amount of greenish-yellow precipitate was quite small. Reduction of 10 g. lots of specimens of Bandrowski's dinitrobenzidine, melting at 225—226°, 233°, and 237° (uncorr.), gave 1·9, 1·1, and 0·0 g. of "quinoxaline" respectively. The crystals appeared as radiating bunches of needles when examined under

the microscope, and melted in the crude state at 292—300°. The product crystallised readily from salicylaldehyde (originally used as a reagent to detect a free amino-group) in long, thin, straw-coloured plates, m. p. 308—309° (uncorr.). Admixture with an authentic specimen of Strakosch's quinoxaline did not depress this m.p. (Cain, Coulthard, and Micklethwait, *loc. cit.*; Brady and McHugh, *loc. cit.*) (Found: N, 10·7. Calc.: 10·0%). The mother-liquors from this crystallisation were dark coloured, indicating that the salicylaldehyde had reacted with the green impurities in the crude quinoxaline (see below).

(b) *At* 100°. In earlier experiments, condensation was attempted using excess of benzil in glacial acetic acid at 100°. In most cases, no precipitation occurred, even on scratching. Dilution with water produced a gummy deposit, from which dilute alcohol extracted a yellowish-green powder, soluble in glacial acetic acid, xylene, benzene, chloroform, and acetone, but obviously a mixture with a m. p. range of about 30°.

A very marked reaction occurred when the product was heated with salicylaldehyde, water being eliminated.

Condensation of 3 : 3′ : 4 : 4′-*Tetra-aminodiphenyl with Benzil.*—To 1 g. of tetra-amine dissolved in 15 c.c. of glacial acetic acid was added a solution of 2 g. of benzil in 5 c.c. of the same solvent. A precipitate was formed suddenly, and this, when viewed under the microscope, appeared as stout needles. Alcohol was added, the solid filtered, re-heated with alcohol, and then dried at 100°. The cream-coloured powder (m. p. crude, 303—306°) separated from salicylaldehyde in straw-coloured plates, m. p. 308° (Found: N, 10·7%). It was very sparingly soluble in glacial acetic acid and acetone, more soluble in benzene, readily soluble in chloroform, and crystallised well from xylene in parallelograms, m. p. 308° (uncorr.), 313° (corr.).

Colour Reactions with Concentrated Sulphuric Acid.—The benzil condensation products derived both from Bandrowski's and from Strakosch's tetra-amines gave nearly identical purplish-red colorations with concentrated sulphuric acid. The colour is clearly due to the quinoxaline structure, and not to the possible presence of benzoylbenzylidene groupings, since αβ-diphenylquinoxaline gave a reddish-orange colour, whilst dibenzoylbenzylidenebenzidine merely dissolved to a normal yellow solution, which after a few minutes set to a white mass of benzidine sulphate. The other colours disappear on the addition of water or on exposure to the air (compare Brunner and Witt, *loc. cit.*).

Preparation of 4-*Bromo*-2′ : 3 : 4′-*trinitrodiphenyl.*—The following method proved more satisfactory than that used in Part III of this

series, as it avoided numerous wasteful crystallisations : An intimate mixture of 100 g. of 4-bromo-4′-nitrodiphenyl and 52 g. of potassium nitrate was slowly added to 300 c.c. of concentrated sulphuric acid at 70—80°. The resulting solution was heated at 90° for ½ hour, then cooled and poured into water. Crystallisation of the resulting precipitate from glacial acetic acid gave 4-*bromo*-3 : 4′-*dinitrodiphenyl* as dull white needles, m. p. 135° (Found : Br, 24·8. $C_{12}H_7O_4N_2Br$ requires Br, 24·8%). A mixture of 8 g. of the latter with 4 g. of potassium nitrate was nitrated in 60 c.c. of concentrated sulphuric acid under the above conditions. The product melted at 176° after one crystallisation from glacial acetic acid.

2′ : 3 : 4′-*Trinitro*-4-*aminodiphenyl*.—4-Bromo-2′ : 3 : 4′-trinitrodiphenyl (3 g.) was heated with saturated alcoholic ammonia (15 c.c.) in a sealed tube at 150° for 8—10 hours. The product was filtered off, dried, and crystallised from glacial acetic acid. It formed yellowish-orange needles, m. p. 192—193° (Found : N, 18·7. $C_{12}H_8O_6N_4$ requires N, 18·4%). This procedure proving very tedious, the following modification was attempted : 20 G. of 4-bromo-2′ : 3 : 4′-trinitrodiphenyl were dissolved in 200 c.c. of boiling nitrobenzene, and a current of dry ammonia was passed through the solution for 2 hours. A yellow solid soon began to separate, and, after cooling, it was collected, washed with benzene, dried, and crystallised from phenol–alcohol, forming bright yellow needles, m. p. 256—257° (Found : N, 17·0. $C_{24}H_{13}O_{12}N_2$ requires N, 16·6%). The analysis and the fact that the substance separates unchanged after being heated with salicylaldehyde prove it to be 4 : 4′-*bis*-op-*dinitrophenyl*-2 : 2′-*dinitrodiphenylamine* (V). Its low solubility in solvents prevented a determination of its molecular weight.

Action of Ammonia upon Boiling Nitrobenzene Solutions of other Halogeno-nitro-compounds.—(*a*) Picryl chloride (10 g.) was dissolved in boiling nitrobenzene (50 c.c.), and ammonia passed in for 2 hours, although solid had begun to separate very soon. The mixture was cooled and the resulting solid was crystallised from glacial acetic acid and identified as trinitroaniline, m. p. 187—188°.

(*b*) 1-Chloro-2 : 4-dinitrobenzene (20 g.), treated similarly (50 c.c. of nitrobenzene), also gave a precipitate, which separated from glacial acetic acid, and had m. p. 180—182°. It was thus 2 : 4-dinitroaniline.

(*c*) 2 : 5-Dichloronitrobenzene (10 g.) dissolved in 25 c.c. of boiling nitrobenzene was apparently unaffected by ammonia.

(*d*) 4 : 4′-Dibromo-2 : 3′-dinitrodiphenyl was partially converted into the corresponding bromo-amino-compound under the above conditions.

Isolation of 2 : 5 : 3′-*Trinitrobenzidine.*—The crude hydrolysis product resulting from a nitration of 70 g. of 2-nitrodiacetylbenzidine was boiled with dilute sulphuric acid, the extract filtered, allowed to crystallise, and the resulting *sulphate* again crystallised from dilute sulphuric acid. It was ground with aqueous ammonia, and the liberated base crystallised three times from phenol–alcohol, dark red needles, m. p. 276°, being obtained (Found : N, 21·6. $C_{12}H_9O_6N_5$ requires N, 21·9%).

The *diacetyl* derivative was a yellow substance, m. p. above 300°.

4 : 4′-*Dibromo*-2 : 5 : 3′-*trinitrodiphenyl.*—A solution of trinitrobenzidine (3·2 g.) in 20 c.c. of concentrated sulphuric acid was diazotised in the usual manner by 1·4 g. of solid sodium nitrite. The solution was diluted by the addition of 100 g. of ice, and filtered; 3 c.c. of bromine dissolved in 12 c.c. of hydrobromic acid were added, and the oily *perbromide* which separated solidified after 15 minutes, and was filtered off. Decomposition by heating with 40 c.c. of glacial acetic acid proceeded smoothly, and gave rise to a cream-coloured, crystalline precipitate of 4 : 4′-*dibromo*-2 : 5 : 3′-*trinitrodiphenyl*, which separated from about 250 c.c. of glacial acetic acid in wads of needles, m. p. 251—252°. The substance reacted readily with piperidine to give the 4 : 4′-*dipiperidino*-compound, which crystallised from rectified spirit in matted needles, m. p. 160° (Found : N, 15·8. $C_{22}H_{25}O_6N_5$ requires N, 15·4%).

Nitration of 4 : 4′-*Dibromo*-2 : 3′-*dinitrodiphenyl.*—When a solution of this compound in nitric acid (*d* 1·5) was allowed to stand, according to Lellmann's instructions, it remained unaffected. 3 G. of the dinitro-compound in 30 c.c. of a mixture (1 : 5 by vol.) of concentrated sulphuric acid and nitric acid (*d* 1·5) were left for 20 hours. Water was then added, and the precipitate extracted with a large bulk of alcohol. The residue crystallised from toluene in colourless needles, m. p. 176—177°, and reacted very vigorously with piperidine, even in the cold, to give the orange-coloured 4-*bromo*-2 : 3′ : 5′-*trinitro*-4′-*piperidinodiphenyl*, which, after being crystallised from much glacial acetic acid, melted at 194° (Found : N, 12·5. $C_{17}H_{15}O_6N_4Br$ requires N, 12·4%).

3 : 4′-*Dinitro*-4-*anilinodiphenyl.*—This substance was obtained by heating 4-bromo-3 : 4′-dinitrodiphenyl with excess of aniline at the b. p. of the latter for 5 minutes. It separated from glacial acetic acid in orange leaflets, m. p. 155—156°.

3 : 2′ : 4′-*Trinitro*-4-*anilino- and* -4-*methylanilino-diphenyl.*—These were readily obtained by heating 4-bromo-3 : 2′ : 4′-trinitrodiphenyl with excess of aniline and methylaniline respectively. The *anilino*-derivative crystallises from glacial acetic acid in orange-red leaflets,

m. p. 190—191°, and the *methylanilino*-derivative from the same solvent in deep red leaflets, m. p. 212°.

Part of the expenses of this investigation were met by grants allocated to two of us by the Chemical Society, and one of us (R. J. W. Le F.) is indebted to the Advisory Committee of the Department of Scientific and Industrial Research for a maintenance grant.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, July 25th,* 1927.]

CCCXII.—*The Preparation of* 2 : 5-*Dihydroxybenzaldehyde* (*Gentisaldehyde*).

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

NEUBAUER and FLATOW (*Z. physiol. Chem.*, 1907, **52**, 375) prepared 2 : 5-dihydroxybenzaldehyde by the oxidation of salicylaldehyde, but the present method with *m*-hydroxybenzaldehyde as initial material gives an improved yield of a less crude product.

A solution of *m*-hydroxybenzaldehyde (61 g.) and sodium hydroxide (25 g.) in water (400 c.c.), while being vigorously stirred and kept at 30—35°, is treated simultaneously from separate dropping-funnels with aqueous solutions of potassium persulphate (150 g. in 1500 c.c.) and sodium hydroxide (200 c.c.; 40%), the additions being made during 90 minutes at such rates that the mixture is always alkaline. After 36 hours' standing, the deep brown solution is rendered faintly acidic (Congo paper) with concentrated hydrochloric acid, and unchanged *m*-hydroxybenzaldehyde (31 g.) is extracted by ether. The solution is then strongly acidified (350 c.c. of concentrated hydrochloric acid) and heated slowly to 70°, the dark brown, amorphous precipitate (5 g.), which forms gradually, being filtered off. (This substance, which chars above 330°, is almost insoluble in all organic solvents except boiling glacial acetic acid, but readily soluble in aqueous sodium carbonate; it contains the aldehyde group, as shown by formation of a p-*nitrophenylhydrazone* which gives the characteristic magenta colour with alkalis, and invariably constitutes about 40% of the yield.) The 2 : 5-dihydroxybenzaldehyde is extracted from the filtrate by ether, the ether is removed by evaporation, and the residue extracted by benzene; yield 13 g. (m. p. 89—92°). The substance crystallises from benzene in bright yellow needles, containing solvent of crystallisation, which rapidly effloresce at the ordinary temperature, leaving yellow needles, m. p. 98—99° (Tiemann and Müller, *Ber.*,

1881, **14**, 1986, give m. p. 99°). The aqueous solution gives a green colour with ferric chloride and red with sodium hydroxide. Identity was established with 2 : 5-dihydroxybenzaldehyde prepared by Neubauer and Flatow's method (*loc. cit.*), in which the corresponding yield of crude product was 12 g. (m. p. 83—90°). Substitution of ammonium for potassium persulphate, reduction in time of keeping, and oxidation at higher temperatures all produced lower yields.

2 : 5-Dihydroxybenzaldehyde could not be obtained from 2-nitro-5-hydroxybenzaldehyde by reduction, diazotisation, and any variation of decomposition procedure, although Sandmeyer treatment of the diazo-solution afforded 30% yields of 2-chloro- or 2-bromo-5-hydroxybenzaldehyde.

Derivatives. The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in brick-red needles, m. p. 256—257° (decomp.) (Found : N, 15·6. $C_{13}H_{11}O_4N_3$ requires N, 15·4%). The *dibenzoate* separates from alcohol in slender, colourless needles, m. p. 106—107° (Found : C, 72·5; H, 4·1. $C_{21}H_{14}O_5$ requires C, 72·8; H, 4·0%), and is readily hydrolysed by cold 20% aqueous sodium hydroxide. The p-*nitrophenylhydrazone* of the dibenzoate crystallises from glacial acetic acid in fine, orange needles, m. p. 272° (Found : N, 9·0. $C_{27}H_{19}O_6N_3$ requires N, 8·7%).

Methylation in 10% aqueous sodium hydroxide solution with methyl sulphate (2 mols.) gives the dimethyl ether, which crystallises from dilute alcohol in colourless needles, m. p. 51° (Tiemann and Müller, *loc. cit.*, give m. p. 51°), and forms a p-*nitrophenylhydrazone*, red needles, m. p. 216° (Found : N, 14·7. $C_{14}H_{14}O_4N_3$ requires N, 14·6%), from glacial acetic acid. In this methylation a monomethyl ether may be isolated, after extraction of the dimethyl ether, by acidification and steam-distillation; it passes over and remains as a colourless oil with a vanillin-like odour, and gives a blue-black colour with ferric chloride and a bright yellow solution with aqueous sodium hydroxide, both tests being characteristic of 5-methoxysalicylaldehyde (Tiemann and Müller, *loc. cit.*); the p-*nitrophenylhydrazone* crystallises from glacial acetic acid in bright orange needles, m. p. 206° (Found : N, 15·4. $C_{13}H_{12}O_4N_3$ requires N, 15·3%).

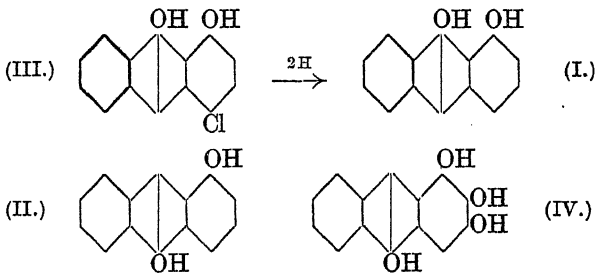
The authors thank the Department of Scientific and Industrial Research for a grant to one of them (H. G. B.), and the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 6th*, 1927.]

CCCXIII.—*The Determination of the Structure of α-Hydroxyanthranols.*

By ALBERT GREEN.

THE reduction of an α-hydroxyanthraquinone to the corresponding anthranol may occur in two ways: *e.g.*, 1-hydroxyanthraquinone may give 1 : 9-dihydroxyanthracene (I), 1 : 10-dihydroxyanthracene (II), or a mixture of these two.



By the reduction of alizarin 2-methyl ether, Miller and Perkin (J., 1925, **127**, 2684) obtained a mixture of the two possible isomeric anthranols, and were able to assign structures to them by observing the differences in the resistance of the derived benzanthrones to methylation. The use of the benzanthrone condensation in the determination of the structures of reactive substances such as the anthranols has disadvantages: purification of the products is tedious, and the yields are very small. Miller and Perkin (*loc. cit.*) themselves suggest that the poor yields are a result of the anthranols suffering alteration during heating with sulphuric acid for 1 hour at 125—130°. However, in a later paper (Cross and Perkin, this vol., p. 1297) improved methods of effecting the benzanthrone condensation are described.

The present method for deciding whether an anthranol is of type (I) or of type (II) depends on its reaction with thionyl chloride, which takes place at the ordinary temperature. It has been shown (J., 1924, **125**, 1450; 1926, 2198; this vol., pp. 500, 554) that two *ortho*-hydroxyl groups of a phenol always react with thionyl chloride to give a thionyl derivative, but that a similar compound is not given by *meta*- or *para*-dihydric phenols (J., 1926, 1428; this vol., p. 500). In view of the well-established resemblance between reactions shown by certain substituents in the *peri*-position (I) and those of the same groups in the *ortho*-position, it was anticipated that a compound of type (I) would yield a thionyl derivative, whereas one of type (II) would not.

These anticipations were verified by examining, in the first place,

the action of thionyl chloride on two substances of known structure, 1 : 8- and 1 : 5-dihydroxynaphthalene. When the former, in carbon disulphide–pyridine solution, is treated with the theoretical quantity of thionyl chloride it gives 1 : 8-*thionyldihydroxynaphthalene* in quantitative yield. The isomeric 1 : 5-dihydroxy-compound, on the contrary, does not give a thionyl derivative: all the methods of preparation previously described (*loc. cit.*) were used, and in every case the products were complex mixtures which always contained chlorine.

The method was then applied to three anthranols. Two of these, 1-hydroxyanthranol and 4-*chloro*-1-*hydroxyanthranol*, yield thionyl derivatives, and are therefore 1 : 9-dihydroxyanthracene (I) and 4-*chloro*-1 : 9-*dihydroxyanthracene* (III) respectively. In preparing the latter by reduction of 4-chloro-1-hydroxyanthraquinone, it was necessary to avoid over-reduction, which readily led to the replacement of the chlorine atom by hydrogen, with production of 1 : 9-dihydroxyanthracene (I).

The products of four experiments with anthragallol anthranol and thionyl chloride were all complex chlorine-containing mixtures, thus indicating that this anthranol is not 1 : 2 : 3 : 9-tetrahydroxyanthracene—for this would be expected to give a chlorine-free dithionyl derivative, since anthragallol itself yields 2 : 3-thionylanthragallol (J., 1926, 2202)—but is 1 : 2 : 3 : 10-tetrahydroxyanthracene (IV). This conclusion, which is based on negative evidence only, is contrary to that reached by Cross and Perkin (*loc. cit.*).

The anthranols used in this investigation were prepared from the corresponding anthraquinones by the method of Liebermann and Mamlock (*Ber.*, 1905, **38**, 1795), with tin and hydrochloric acid in acetic acid solution as reducing agent. This method was preferred to the more economical one of Breare and Perkin (J., 1923, **123**, 2606), who used a hydrochloric acid solution of stannous chloride, because the products were more easily purified.

The compounds described herein differ from the thionyl derivatives examined previously (*loc. cit.*) in that the thionyl group forms part of a six-atom ring, and is less reactive than one forming part of a heterocyclic structure of five atoms.

EXPERIMENTAL.

Preparation of Materials.—1 : 8-*Dihydroxynaphthalene.* A commercial specimen labelled "pure" contained more than 70% of impurities. The naphthol was eventually obtained pure by two methods: (I) A hot solution of the mixture in acetic anhydride and pyridine, on cooling, deposited practically pure 1 : 8-diacetoxy-

naphthalene. After one recrystallisation from acetic anhydride, this formed small, white plates of constant m. p. 155° (Erdmann, *Annalen*, 1888, 247, 359, gives 147—148°) (Found: $CH_3 \cdot CO$, 35·7. Calc.: 35·3%). The acetyl derivative was hydrolysed by the rapid addition of hydrochloric acid to its solution in hot acetic acid. After removal of some tarry matter by filtration through asbestos, a warm saturated solution of sulphur dioxide was added, and 1 : 8-dihydroxynaphthalene separated as hair-like, white needles, m. p. 144° (Found: C, 74·8; H, 5·1. Calc.: C, 75·0; H, 5·0%). (II) The impurities were very sparingly soluble in cold acetic acid, and were removed by fractional crystallisation. The acetic acid solutions, when diluted with water, yielded the naphthol as small, greyish-white crystals, which, after drying over sulphuric acid, melted at 142—143° (Found: C, 74·8; H, 5·2%). 1 : 8-Dihydroxynaphthalene dissolves in concentrated sulphuric acid with a greenish-gold colour, and its colourless solution in alcohol becomes dark green on the addition of ferric chloride.

The anthraquinones, which were converted into the anthranols, were obtained by the hydrolysis of the purified acetyl derivatives (compare J., 1926, 1431, 2199).

1 : 9-*Dihydroxyanthracene* (1-*Hydroxyanthranol*). This was obtained, by treating the hot acetic acid solution of the diacetate with hydrochloric acid, as faintly yellow, square plates, m. p. 142° (Found: C, 79·9; H, 4·9. Calc.: C, 80·0; H, 4·8%). The diacetate separated from a mixture of acetic anhydride and pyridine in short, pale yellow, six-sided prisms, m. p. 211° (Found: $CH_3 \cdot CO$, 29·3. Calc.: $CH_3 \cdot CO$, 29·3%).

4-*Chloro*-1 : 9-*dihydroxyanthracene* (4-*Chloro*-1-*hydroxyanthranol*). Owing to the ease with which 4-chloro-1-hydroxyanthraquinone was reduced to 1 : 9-dihydroxyanthracene, it was necessary to control the reduction carefully. The addition of hydrochloric acid to the acetic acid solution was stopped as soon as a test portion, added to excess of caustic soda, no longer showed a trace of the red colour of the sodium salt of the hydroxyanthraquinone (about 3 minutes). The solution was then rapidly decanted from the residual tin and cooled. The acetylated product, after recrystallisation from absolute alcohol, yielded 4-*chloro*-1 : 9-*diacetoxyanthracene* as rosettes of faintly yellow, fine needles, m. p. 157° [Found: Cl, 10·7; $CH_3 \cdot CO$, 28·5. $C_{14}H_7O_2Cl(CH_3 \cdot CO)_2$ requires Cl, 10·8; $CH_3 \cdot CO$, 28·2%]. The hot acetic acid solution of these, when treated with hydrochloric acid, deposited 4-*chloro*-1 : 9-*dihydroxyanthracene* as pale greenish-yellow needles of constant m. p. 170—171° (Found: Cl, 14·5; *M*, cryoscopic in naphthalene, 245, 250. $C_{14}H_9O_2Cl$ requires Cl, 14·5%; *M*, 244·5), giving a bright greenish-gold solution

in concentrated sulphuric acid. Its solution in aqueous caustic soda is bright yellow, but on standing in air this is rapidly oxidised to the wine-red solution characteristic of the sodium salt of 4-chloro-1-hydroxyanthraquinone. In alcohol, the anthranol gives a pale greenish-yellow solution which becomes golden-brown on the addition of ferric chloride.

When 3·2 g. of 4-chloro-1 : 9-dihydroxyanthracene were reduced further by the method of Liebermann and Mamlock (*loc. cit.*) during 40 minutes, the product contained less than 1% of chlorine. Its solution in a mixture of warm pyridine and acetic anhydride deposited 2·1 g. of 1 : 9-diacetoxyanthracene, m. p. 208—209°, which after one recrystallisation from the same mixture melted at 210—211°, either alone or mixed with an authentic specimen (Found : $CH_3{\cdot}CO$, 29·6. Calc. : 29·3%).

The thionyl derivatives were prepared by the method adopted for 1 : 2-thionyldihydroxyanthracene (this vol., p. 557).

1 : 8-*Thionyldihydroxynaphthalene* (5·5 g. from 5·3 g. of the naphthol) separated from carbon disulphide in small, pearl-grey crystals, m. p. 97° (Found : C, 58·6; H, 2·9; S, 15·5; *M*, cryoscopic in naphthalene, 218, 210. $C_{10}H_6O_3S$ requires C, 58·3; H, 2·9; S, 15·5%; *M*, 206). It is stable to moisture and a specimen which had stood in air for 9 weeks showed no change in m. p. or in sulphur content. Cold aqueous caustic potash has no appreciable effect on the thionyl compound, but a hot alcoholic solution decomposes it with the production of a pale amethyst colour and the deposition of potassium sulphite. The thionyl compound dissolves in concentrated sulphuric acid with a dull amethyst colour, which changes to the greenish-gold of the naphthol when the solution is heated.

1 : 9-*Thionyldihydroxyanthracene* was obtained (5·0 g. from 4·8 g. of anthranol) from carbon disulphide as pale greenish-yellow plates, m. p. 115° (decomp.) (Found : C, 65·7; H, 3·2; S, 12·7; *M*, cryoscopic in naphthalene, 260, 264. $C_{14}H_8O_3S$ requires C, 65·6; H, 3·1; S, 12·5%; *M*, 256). It gives a greenish-gold solution in cold concentrated sulphuric acid; it is not appreciably soluble in cold caustic soda, but yields a light golden-brown solution on warming. The addition of ferric chloride to its pale yellow solution in alcohol produces no change.

4-*Chloro*-1 : 9-*thionyldihydroxyanthracene* crystallised from carbon disulphide in pale greenish-yellow plates, m. p. 123—124° (decomp.), 4·0 g. of anthranol yielding the same amount of thionyl derivative (Found : S, 11·2; Cl, 12·0; *M*, cryoscopic in naphthalene, 295. $C_{14}H_7O_3ClS$ requires S, 11·0; Cl, 12·2%; *M*, 290·5). The colour reactions are similar to those of 1 : 9-thionyldihydroxyanthracene.

The products obtained by treating 1 : 5-dihydroxynaphthalene with thionyl chloride showed chlorine contents varying from 14 to 22%; those from anthragallol anthranol contained sulphur in amounts varying from 0·7 to 15·6%, and chlorine from 2·1 to 21·5%. In all cases, the reactions and properties of the products pointed to their being complex substances formed by the condensation of several molecules.

The author desires to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed a portion of the cost of this research, and also The British Alizarine Company, Limited, and The Scottish Dyes, Limited, for gifts of materials.

THE EDWARD DAVIES LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

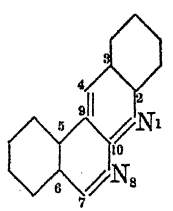
[*Received, August 5th*, 1927.]

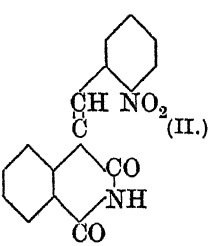
CCCXIV.—*Some Derivatives of* 2 : 3 : 5 : 6-*Dibenzo*-1 : 8-*naphthyridine.*

By ROBERT DOWNS HAWORTH and HERBERT SHEPHERD PINK.

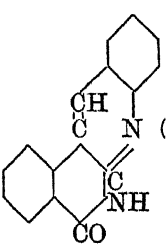
DERIVATIVES of 2 : 3 : 5 : 6-dibenzo-1 : 8-naphthyridine (I) have not been previously described, and a method for their preparation from homophthalimide is now communicated. Dieckmann (*Ber.*, 1914, **47**, 1428) showed that the diethyl ester of homophthalic acid condensed with aldehydes, and homophthalimide is now shown to condense in a similar manner with *o*-nitrobenzaldehyde, giving excellent yields of o-*nitrobenzylidenehomophthâlimide* (II) in pyridine solution in the presence of a trace of piperidine.

(I.)





(II.)

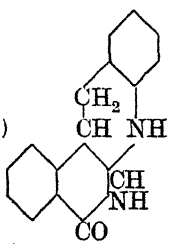


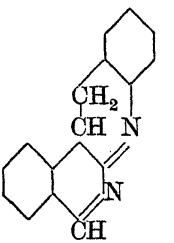
(III.)

This sparingly soluble substance was reduced with stannous chloride in alcoholic solution to 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* (III), which is a pale yellow, very weak base, dissolving in concentrated mineral acids and being precipitated on dilution with water; it possesses marked acidic properties, however, owing to the presence of the *iso*carbostyril

grouping, and on treatment with dilute potassium or sodium hydroxide, bright yellow, sparingly soluble salts were obtained, the *sodium* salt being somewhat more soluble than the *potassium* salt. Owing to the sparing solubility of this ketodibenzodihydronaphthyridine, further reduction was difficult, but zinc dust in glacial acetic acid, saturated with hydrogen chloride, effected reduction to 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* (IV), which is devoid of acidic properties, but readily yields a *monohydrochloride* and an amorphous *nitrosoamine*.

(IV.)





(V.)

A similar series of compounds was obtained from the *N*-alkylated homophthalimides, the 8-β-*phenylethyl* and 8-β-*piperonylethyl* derivatives [as (II), (III), and (IV)] being described.

In attempting to reduce the carbonyl group of the ketodibenzodihydronaphthyridine (III), a small yield of a yellow *base*, $C_{16}H_{12}N_2$, was obtained by electrolytic reduction in alcoholic sulphuric acid solution. The same base was, however, more conveniently prepared (in 20% yield) by heating the keto-compound (III) with phosphorus oxychloride and pentachloride at 180° and reducing the unstable chloro-compound with phosphorus and hydriodic acid at 160—170°, the compound (IV) also being formed. The yellow base, $C_{16}H_{12}N_2$, was sparingly soluble in organic solvents and its dilute solutions exhibited an intense violet fluorescence. The two nitrogen atoms are both tertiary in character, since no nitrosoamine or acetyl derivative can be obtained. It is probably 2 : 3 : 5 : 6-*dibenzo*-4 : 9-*dihydro*-1 : 8-*naphthyridine* (V), for it dissolved in hot dilute hydrochloric acid to give a sparingly soluble *monohydrochloride*, and this monoacidic character is in agreement with the amidine structure suggested.

Experimental.

o-*Nitrobenzylidenehomophthalimide* (II).—Homophthalimide (20 g.), o-nitrobenzaldehyde (20 g.), pyridine (100 c.c.), and piperidine (0·5 c.c.) were boiled until homogeneous, and the heating was continued on the water-bath for 2 hours; the solution became

dark red and the product gradually separated on cooling in pale yellow needles, which recrystallised from pyridine in pale sulphur-yellow needles (35 g.), m. p. 236° (Found: N, 9·6. $C_{16}H_{10}O_4N_2$ requires N, 9·5%). o-*Nitrobenzylidenehomophthalimide* is sparingly soluble in the usual organic solvents, and gives a yellow solution in dilute aqueous sodium hydroxide.

o-*Nitrobenzylidene*-N-β-*phenylethylhomophthalimide* was prepared similarly from *o*-nitrobenzaldehyde and *N*-β-phenylethylhomophthalimide; it crystallised from pyridine in yellow needles, m. p. 146° (Found: N, 7·2. $C_{24}H_{18}O_4N_2$ requires N, 7·0%). o-*Nitrobenzylidene*-N-β-*piperonylethylhomophthalimide*, prepared from *o*-nitrobenzaldehyde and *N*-β-piperonylethylhomophthalimide, crystallised from pyridine in yellow needles, m. p. 176° (Found: N, 6·7. $C_{25}H_{18}O_6N_2$ requires N, 6·2%).

7-*Keto*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* (III).—A mixture of *o*-nitrobenzylidenehomophthalimide (II) (15 g.), stannous chloride (40 g.), and ethyl alcohol (200 c.c.) was saturated with hydrogen chloride and heated on the water-bath for 12 hours. After cooling, the tin double compound was collected, digested with excess of potassium hydroxide solution for ½ hour, cooled, and the bright yellow *potassium* salt decomposed by trituration with dilute hydrochloric acid; the resulting *ketodibenzodihydronaphthyridine* was recrystallised from glacial acetic acid, forming very pale yellow needles (12 g.), m. p. 246—247° (Found: C, 77·9; H, 4·1; N, 11·1. $C_{16}H_{10}ON_2$ requires C, 78·0; H, 4·1; N, 11·4%). It is almost insoluble in water, ether, alcohol, acetone, or benzene, slightly soluble in hot chloroform, and soluble in hot glacial acetic acid or pyridine. It dissolves in concentrated hydrochloric acid, but is reprecipitated on dilution. The potassium salt is almost insoluble in water. The *sodium* salt is slightly soluble in hot water, from which it separates in glistening, bright yellow plates (Found: Na, 8·7. $C_{16}H_9ON_2Na$ requires Na, 8·6%); it is also obtained by boiling the ketodibenzodihydronaphthyridine (III) with methyl-alcoholic sodium hydroxide, no further hydrolysis taking place.

7-*Keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* was obtained from *o*-nitrobenzylidene-*N*-β-phenylethylhomophthalimide by reduction with stannous chloride, as described above. It crystallises from acetic acid in almost colourless needles, m. p. 220° (Found: C, 82·1; H, 5·2. $C_{24}H_{18}ON_2$ requires C, 82·3; H, 5·1%). It is a very weak base, and shows no acidic properties. 7-*Keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* crystallises from glacial acetic acid in pale yellow needles, m. p. 217° (Found: C, 76·0; H, 4·9. $C_{25}H_{18}O_3N_2$ requires C, 76·1; H, 4·6%).

7-*Keto*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* (IV).—o-Nitrobenzylidenehomophthalimide (6 g.) or ketodibenzodihydronaphthyridine (III) (6 g.) was dissolved in glacial acetic acid (100 c.c.), saturated with hydrogen chloride, and heated with a large excess of zinc dust for 3 hours on the water-bath. The mixture was diluted with water, made strongly alkaline with ammonia, extracted with chloroform, the solvent removed, and the residue crystallised first from boiling ethyl alcohol and then from methyl ethyl ketone, colourless needles (0·5 g.), m. p. 250°, being obtained (Found: C, 77·4; H, 5·7. $C_{16}H_{14}ON_2$ requires C, 76·8; H, 5·6%). This substance (IV) is more soluble in organic solvents than the dihydro-compound (III). It is insoluble in sodium hydroxide solution, but dissolves in dilute hydrochloric acid; on concentration the *monohydrochloride* separates in colourless needles, which darken at about 225° and decompose at 270° (Found: Cl, 12·3. $C_{16}H_{15}ON_2Cl$ requires Cl, 12·5%). When its solution in dilute hydrochloric acid was treated with sodium nitrite an amorphous *nitrosoamine* gradually separated. This was extracted with chloroform, the extract washed thoroughly with sodium bicarbonate solution, and the solvent removed; the residue gave Liebermann's test for nitrosoamines. The *picrate*, prepared in alcoholic solution, crystallised from glacial acetic acid in small, yellow needles, m. p. 270° (Found: N, 14·6. $C_{22}H_{17}O_8N_5$ requires N, 14·6%).

7-*Keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine*, obtained by reducing the corresponding dihydro-compound or *o*-nitrobenzylidene-*N*-β-piperonylethylhomophthalimide with zinc dust, as described above, crystallises from ethyl alcohol in colourless needles, m. p. 217° (Found: C, 81·1; H, 6·4. $C_{24}H_{22}ON_2$ requires C, 81·3; H, 6·2%). 7-*Keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* separates from ethyl alcohol in colourless needles, m. p. 211° (Found: C, 75·4; H, 5·7. $C_{25}H_{22}O_3N_2$ requires C, 75·4; H, 5·5%).

2 : 3 : 5 : 6-*Dibenzo*-4 : 9-*dihydro*-1 : 8-*naphthyridine* (V).—The corresponding 1 : 8-dihydroketo-compound (III; 5 g.), phosphorus pentachloride (6 g.), and phosphorus oxychloride (10 c.c.) were heated for 5 hours in a sealed tube at 180°. The oxychloride was removed under diminished pressure, and the solid residue * (7 g.) heated with red phosphorus (1·5 g.) and hydriodic acid (*d* 1·7; 30 c.c.) for 9 hours at 160—170°; the pale greenish-yellow solution, containing long, pale yellow prisms, was diluted with water, boiled, and the sparingly soluble *hydriodide* decomposed by the addition

* The chloro-derivative could not be isolated from this solid residue, as it was rapidly hydrolysed to the keto-compound (III) by water.

of a large excess of ammonia. The base was extracted with chloroform, the extract dried, the solvent removed, the residual solid dissolved in hot dilute hydrochloric acid, filtered, and cooled; the hydrochloride separated in pale orange needles, which were collected, dissolved in water, and decomposed with sodium hydroxide; the resulting yellow base crystallised from ethyl alcohol in pale yellow needles (0·9 g.), m. p. 232° (Found: C, 82·4, 82·8; H, 5·4, 5·5. $C_{16}H_{12}N_2$ requires C, 82·8; H, 5·2%). It is sparingly soluble in ether, light petroleum, or benzene, fairly soluble in hot alcohol, and readily soluble in chloroform, glacial acetic acid, or hot dilute mineral acids. Its alcoholic solutions are almost colourless, with an intense violet fluorescence. The *monohydrochloride* crystallises from water in pale yellow needles which darken at about 240° and gradually decompose at higher temperatures (Found: Cl, 12·9. $C_{16}H_{13}N_2Cl$ requires Cl, 13·3%). The base does not yield a nitrosoamine or acetyl derivative, and could not be further reduced by zinc dust and acids.

THE DYSON PERRINS LABORATORY, OXFORD.
ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE. [*Received, August 9th*, 1927.]

CCCXV.—*New Reference Compounds in the Sugar Group. The Methylamides of* d-, l-, *and* i-*Dimethoxysuccinic Acids and of* l-*Arabo- and* i-*Xylo-trimethoxyglutaric Acids.*

By WALTER NORMAN HAWORTH and DAVID IDRIS JONES.

COMPARED with other groups of organic substances, the carbohydrates have hitherto been provided with few fundamental reference compounds which can serve as final standards for the complete identification of the normal and labile forms of sugars through their oxidation derivatives.

The most readily accessible oxidation derivatives of the methylated aldoses are the lactones of the corresponding acids, and most of these lactones are crystalline and give characteristic phenylhydrazides. A lactone of the δ- or amylene-oxide series can be sharply differentiated from the corresponding member of the γ- or butylene-oxide series by reason of its different rate of hydrolysis as revealed by physical methods (Drew, Goodyear, and Haworth, this vol., p. 1237; also forthcoming paper by Carter, Haworth, and Robinson).

The ultimate basis on which the constitution of each of these

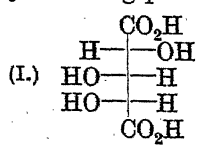
lactones rests is that of the simple dibasic acids to which they give rise on oxidation. Our further study of these lactones by methods of degradative oxidation has revealed the need of a final standard of comparison of these oxidation products with the derivatives of the stereoisomeric forms of tartaric acid and of trihydroxyglutaric acid. Methylated derivatives of these acids do not lend themselves to easy recognition. Crystalline amides of some of these acids have been prepared and examined (Hirst and Purves, J., 1923, **123**, 1352; Hirst and Robertson, J., 1925, **127**, 358) and their physical properties are of some service for the purpose of identification, but inasmuch as these amides melt with decomposition at high temperatures, their utility as standard reference substances suffers by reason of the untrustworthiness of their application in mixed m. p. determinations.

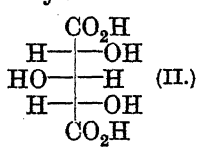
A search for new crystalline derivatives of the stereoisomeric forms of dimethoxysuccinic acid and of trimethoxyglutaric acid has led us finally to adopt as our standards the crystalline methylamides. These substances melt at a definite temperature, solidify on cooling, and then remelt at the same temperature as before, and they undergo no change either of condensation or decomposition at this elevated temperature.

Thus *l*-tartaric acid, prepared by Pasteur's method from racemic acid, was esterified to methyl *l*-tartrate, and methylation by the usual methods gave rise to *methyl* l-*dimethoxysuccinate*. The latter was converted with the aid of pure methylamine into l-*dimethoxysuccinomethylamide*. Similar methods applied to the corresponding *d*- and *i*-tartaric acids furnished the remaining stereoisomeric forms of the above methylamide. Their physical properties are tabulated below for comparison :

	M. p.	$[\alpha]_D$ in water.
d-Dimethoxysuccinomethylamide	205°	+132·6°
l- " " "	205	−131·8
i- " " "	210	Zero

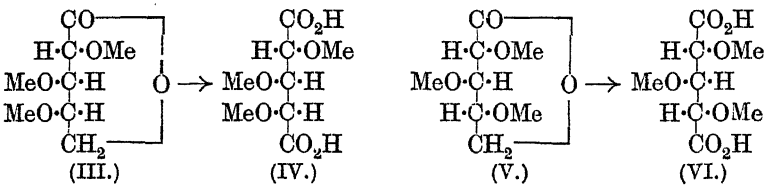
Of the four stereoisomeric forms of trihydroxyglutaric acid, two are most frequently encountered as oxidation products in the sugar group, namely, *l*-arabotrihydroxyglutaric acid (I) and *i*-xylotrihydroxyglutaric acid (II), which are obtained, respectively, from the naturally occurring pentoses, arabinose and xylose :





Both these forms are represented in the cases which we have studied. Thus, *l*-trimethyl δ-arabonolactone (III), prepared from normal methylated arabinose, has been oxidised with nitric acid and

found to give rise almost exclusively to *l*-arabotrimethoxyglutaric acid (IV). Conversion of this into the methyl ester was followed by treatment with methylamine, which gave a quantitative yield of l-*arabotrimethoxyglutaromethylamide*, m. p. 172°, $[\alpha]_D$ + 59·9°. The corresponding amide was similarly prepared. Again, the oxidation of trimethyl δ-xylonolactone (V) gave an almost quantitative yield of *i*-xylotrimethoxyglutaric acid (VI), which was converted into i-*xylotrimethoxyglutaromethylamide*, m. p. 167—168°, and also into the corresponding amide.



The isolation of these products furnishes a proof of the constitution of the two δ-lactones (III and V), and also confirms the amylene-oxide structure of the normal forms of trimethyl arabinose and trimethyl xylose.

Experimental.

d-*Dimethoxysuccinomethylamide.*—Methyl *d*-dimethoxysuccinate having $[\alpha]_D^{18°}$ + 79·9° in methyl alcohol (c = 2·04) (compare Purdie and Barbour, J., 1901, **79**, 973) was prepared from *d*-tartaric acid. The ester was dissolved in dry methyl alcohol saturated with methylamine. The solution was kept for several days, and on concentration yielded long, colourless needles which, recrystallised from light petroleum (b. p. 60—80°), had m. p. 205°; $[\alpha]_D^{15°}$ + 132·6° in water (c = 1·95); yield 90% (Found: C, 47·0; H, 7·8; N, 13·5; OMe, 29·5. $C_8H_{16}O_4N_2$ requires C, 47·05; H, 7·8; N, 13·7; OMe, 30·4%).

Methyl l-*Dimethoxysuccinate.*—A specimen of *l*-tartaric acid [m. p. 167—170°; $[\alpha]_D^{18°}$ − 14·6° in water (c = 3·15)] was prepared by fermentation methods from racemic acid, and esterified in the presence of methyl alcohol containing 3% of hydrogen chloride; yield 95%. The methyl *l*-tartrate was methylated by Purdie's reagents and gave a colourless liquid, b. p. 83°/0·07 mm.; $n_D^{18°}$ 1·4345; $[\alpha]_D^{18°}$ − 78·8° in methyl alcohol (c = 3·12) (0·2340 G. required 22·9 c.c. *N*/10-sodium hydroxide. Calc.: 22·75 c.c.) (Found: C, 46·8; H, 7·0; OMe, 58·3. Calc.: C, 46·6; H, 6·8; OMe, 60·2%).

l-*Dimethoxysuccinomethylamide.*—The methyl *l*-dimethoxysuccinate was dissolved in dry methyl alcohol, saturated with methylamine, and the solution concentrated after 40 hours; a crystalline mass then filled the containing vessel. The *methylamide* was

recrystallised from ethyl acetate; the long needles thus obtained melted at 205°, solidified on cooling, and remelted at the same temperature; $[\alpha]_D^{17^\circ}$ — 131·8° in water ($c = 1{\cdot}61$); yield 82% (Found: C, 46·8; H, 7·7; N, 13·8; OMe, 28·4. $C_8H_{16}O_4N_2$ requires C, 47·05; H, 7·8; N, 13·7; OMe, 30·4%).

The crystalline l-*dimethoxysuccinamide* was also made in the usual way and isolated as colourless needles which became coloured at 250°, dark at 270°, melted at 278°, and decomposed violently at 294°, a behaviour which was identical with that exhibited by the *d*-isomeride (Found: C, 40·8; H, 6·6; N, 15·8; OMe, 33·5. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·8; N, 15·9; OMe, 35·2%).

i-*Dimethoxysuccinomethylamide.*—*meso*Tartaric acid was esterified in presence of methyl alcohol and methylated with Purdie's reagents, giving flat plates, m. p. 68°. This specimen of methyl *i*-dimethoxysuccinate was dissolved in methyl alcohol, saturated with methylamine, and the solution kept for 3 days, during which long needles separated, further crops being obtained by concentration. The *methylamide* was recrystallised from ethyl acetate; m. p. 210°; zero rotation in water ($c = 1{\cdot}6$); yield 97% (Found: C, 46·9; H, 8·0; N, 13·6; OMe, 29·8. $C_5H_{16}O_2N_2$ requires C, 47·1; H, 7·8; N, 13·7; OMe, 30·4%).

Oxidation of Trimethyl δ-Xylonolactone.—A specimen of this lactone, m. p. 55° (Haworth and Westgarth, J., 1926, 886) was oxidised with nitric acid (*d* 1·42) by heating the solution in a water-bath at 70—75° for ¾ hour, and thereafter for 3 hours at 90—95°. The removal of the nitric acid was effected in the usual way and the syrupy oxidation product collected, esterified with dry methyl alcohol containing 4% hydrogen chloride, the solution neutralised with silver carbonate, and the solvent evaporated. The liquid product was dissolved in ether, dried, and distilled; b. p. 102—104°/0·09 mm.; n_D 1·4402; the yield was quantitative. That this product was methyl *i*-trimethoxyglutarate was shown by conversion into the crystalline amide (yield over 60%); the crystals turned slightly brown at 195° and melted quickly at 195—198° to a blue liquid. The rotation was zero. Comparison with an authentic specimen of *i*-xylotrimethoxyglutaramide proved its identity.

i-*Trimethoxyglutaromethylamide.* — The above ester was dissolved in methyl alcohol, saturated with methylamine, and kept for 15 hours; crystals then separated, and further crops were obtained by concentration of the solution. The *methylamide* crystallised from ethyl acetate in silky needles, m. p. 167—168°, solidifying and then remelting at 167° (yield 85%). The rotation was zero (Found: C, 48·4; H, 8·4; N, 10·85; OMe, 36·3. $C_{10}H_{20}O_5N_2$ requires C, 48·35; H, 8·1; N, 11·2; OMe, 36·4%).

Oxidation of Trimethyl δ-Arabonolactone.—This lactone (m. p. 45°; $[\alpha]_D^{21°}$ + 179·5° in water) was prepared from crystalline trimethyl β-methylarabinoside as described by Drew and Haworth (this vol., p. 778). The lactone (5 g.) was dissolved in 40 c.c. of nitric acid (*d* 1·42), and the solution heated on the water-bath. The oxidation commenced at 90°, and during a period of 5 hours the evolution of brown fumes was continuous; the reaction then ceased. The nitric acid was removed by dilution with water followed by continuous distillation of the dilute acid at 40°/15 mm.; methyl alcohol was added to, and distilled from, the residue, and the resulting syrup was digested with a solution containing 80 c.c. of methyl-alcoholic hydrogen chloride (3%). Thereafter, the mineral acid was removed by neutralisation with silver carbonate, and the product, a pale yellow syrup (5·8 g.), was distilled, b. p. 105°/0·14 mm.; $n_D^{15°}$ 1·4365; yield 5·25 g. The methyl trimethoxyglutarate showed $[\alpha]_D^{20°}$ + 37·6° in water (*c* = 2·52) and $[\alpha]_D^{18°}$ + 41·2° in methyl alcohol (*c* = 1·31) (Found: C, 47·6; H, 7·3; OMe, 58·35. Calc.: C, 48·0; H, 7·2; OMe, 62·0%). This product (0·5 g.) was dissolved in dry methyl alcohol (6 c.c.), and the solution saturated with dry ammonia. On keeping, a crystalline amide separated, (yield 0·4 g.), m. p. 228—229°. Recrystallisation from methyl alcohol raised the m. p. to 230° (decomp.) (Found: C, 43·7; H, 7·2; N, 13·0; OMe, 40·6%).

l-*Arabotrimethoxyglutaromethylamide.*—Another specimen (0·46 g.) of the preceding ester was dissolved in methyl alcohol (6 c.c.) and saturated with methylamine. After keeping for 3 days at the ordinary temperature the solution was concentrated under diminished pressure and gave crystals (yield 0·45 g.) of the *methylamide.* Recrystallisation from ethyl acetate gave radiating needles (m. p. 172°), solidifying on cooling and remelting at the same temperature; $[\alpha]_D^{18°}$ + 59·9° in water (*c* = 1) (Found: C, 48·3; H, 8·2; N, 10·9; OMe, 35·6. $C_{10}H_{20}O_5N_2$ requires C, 48·35; H, 8·1; N, 11·2; OMe, 36·4%).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCCXVI.—*The Photochemical Oxidation of Alcohols by the Dichromate Ion.*

By EDMUND JOHN BOWEN and CHARLES WILLIAM BUNN.

THE photochemical oxidation of alcohols by the dichromate ion has been studied by Plotnikov (*Z. wiss. Phot.*, 1919, **19**, 40; *Z. Elektrochem.*, 1926, **32**, 13). The aim of the present work was to

obtain measurements under as great a variety of conditions as possible, and to make measurements of the quantum efficiency.

Four lamps were used for different parts of the work: a 1000-c.p. Pointolite lamp, a 1000-watt tungsten-filament lamp, water-cooled, and two quartz–mercury lamps. Copper sulphate solution filters were used to remove infra-red and red radiation, and with the mercury lamps practically monochromatic radiation was obtained with Chance's black glass and cupriammonium sulphate filters.

The reactions were carried out in small quartz cells with plane-polished quartz ends fused on, the cells being fixed in a water thermostat electrically controlled. The energies of the radiations and the absorptions of the solutions were measured with a Moll thermopile calibrated in the usual way with a Hefner lamp.

The following two points were established in the first part of the work: (*a*) The chromate ion in neutral or alkaline solution is photochemically quite insensitive towards the alcohols. The results of Plotnikov (*loc. cit.*), that ammonium chromate is photoactive, are to be explained by partial hydrolysis to dichromate.

(*b*) The photochemical reaction between acid dichromate-ion solutions and alcohols leads to aldehyde formation without deposition of a precipitate. (In neutral solutions a precipitate is thrown down.) A series of measurements made with methyl alcohol solutions showed that the photochemical reaction curve obtained from the estimation of formaldehyde by the method of Schulek (*Ber.*, 1925, **58**, 732) was consistently 20% lower than that obtained from the decrease in dichromate-ion concentration. This was shown experimentally to be due to further oxidation of the formaldehyde, and the photochemical reaction may be represented:

$$Cr_2O_7'' + 8H^{\cdot} + 3CH_3{\cdot}OH \longrightarrow 3CH_2O + 2Cr''' + 7H_2O.$$

In later experiments, the reaction was followed only by estimation of the dichromate-ion concentration, potassium iodide being added and the iodine titrated. The thermal reaction was followed at the same temperature, the reactants being contained in a blackened flask, and the true photochemical change was obtained by subtraction of the (small) thermal rate from the total rate in light.

The results of numerous experiments are summarised as follows. The quantum efficiency is independent of the following four factors: (1) light intensity, over a range of 1 : 80; (2) added acid, above a certain limit; (3) dichromate-ion concentration, between $N/10$ and $N/100$; and (4) temperature, between 15° and 50°.

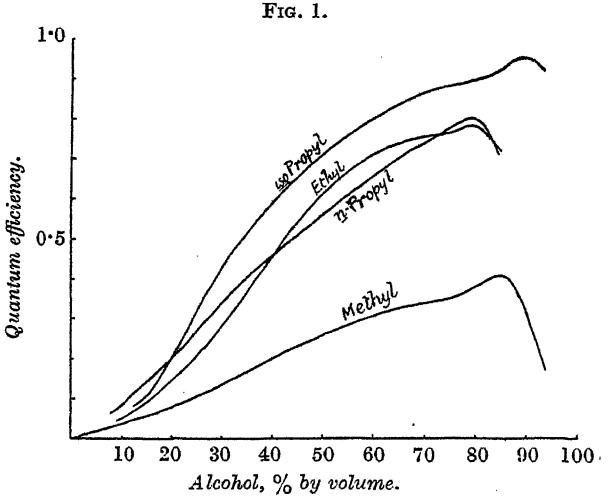
The photochemical reaction curves were determined for a series of alcohol–water mixtures at 15°, the dichromate-ion concentration being maintained at $N/20$ in each mixture, and the acid at $0{\cdot}2N$.

All the curves were linear over a large range of the first part of the reaction, and the slope gave the photochemical rates for the mixtures; these are summarised in Table I, the rates being expressed as the ratio of Cr_2O_7'' ions reduced to quanta absorbed, and plotted in Fig. 1.

TABLE I.

Methyl alcohol.		Ethyl alcohol.		*n*-Propyl alcohol.		*iso*Propyl alcohol.	
Alcohol, % by vol.	Photochemical rate.	Alcohol, % by vol.	Photochemical rate.	Alcohol, % by vol.	Photochemical rate.	Alcohol, % by vol.	Photochemical rate.
10	0·037	10	0·043	10	0·081	15	0·108
20	0·073	20	0·152	15	0·138	30	0·434
30	0·129	30	0·259	30	0·384	50	0·693
40	0·191	40	0·467	40	0·449	70	0·854
50	0·252	50	0·613	50	0·601	80	0·896
60	0·316	60	0·706	60	0·620	85	0·917
70	0·333	70	0·747	70	0·732	89	0·940
75	0·345	75	0·756	80	0·780	94	0·918
80	0·379	80	0·771	85	0·705		
85	0·400	85	0·714	89	0·606		
89	0·351						
94	0·162						
96	0 (fast dark reaction)						

FIG. 1.



As a check on these measurements, which were made in the light from a tungsten-filament lamp, filtered through copper sulphate solution, the quantum efficiency for the series of alcohols at concentrations equal to that of maximum rate was measured in monochromatic light from a quartz lamp: At 3666 Å., *Q.E.* of alcohol: methyl 0·45, ethyl 0·86, *n*-propyl 0·86, *iso*propyl 1·00. At 4200 Å. (approx.), ethyl alcohol 0·89. These results agree with the previous ones within the limit of error, if account be taken of the complete

change of apparatus. The whole absorption band of the dichromate ion in the blue and violet region is therefore equally photoactive.

The variation of reaction rate with diminishing acid concentration was investigated and showed a regular decrease, but the results cannot be simply interpreted since the reaction occurs chiefly in the forward layers of the solution, producing variations in acidity throughout the cell. The reactions were also investigated in neutral solution. In this case, a precipitate is thrown down which is not chromium hydroxide, but which is capable of liberating iodine from potassium iodide. Owing to the scattering of the light by the precipitate, the rate falls off rapidly from the beginning of the exposure, and becomes zero when one-half of the total oxidising power of the dichromate solution is utilised. The simplest explanation of this is the formation of chromate:

$$Cr_2O_7'' + 3CH_3{\cdot}OH + H_2O \longrightarrow 3CH_2O + 2OH' + 2Cr(OH)_3.$$
$$2OH' + Cr_2O_7'' \longrightarrow 2CrO_4'' + H_2O.$$

The nature of the precipitate is obscure. Plotnikov has suggested that it is chromium chromate.

Owing to the falling off of the rate with time in the neutral reactions the initial rates for different alcohol–water mixtures were obtained by calculation from the curves. Table II summarises these initial rates, expressed for convenience as the ratio of rates acid/neutral for each mixture:

TABLE II.

Methyl alcohol.		Ethyl alcohol.		*n*-Propyl alcohol.	
Alcohol, % by vol.	Ratio of rates, acid / neutral	Alcohol, % by vol.	Ratio of rates, acid / neutral	Alcohol, % by vol.	Ratio of rates, acid / neutral
30	2·77	20	2·06	15	2·2
50	2·92	30	2·15	30	2·87
70	2·80	40	2·85	50	3·3
80	2·93	50	3·1	70	3·28
82·5	2·89	70	3·2	80	3·08
85	2·62				
87·5	2·50				
90	3·0				

These measurements are not so accurate as those for acid solutions because of the uncertainty in the estimation of the initial rate. Since the ratio is practically constant, the curves for the neutral reactions are almost identical with those for the acid solutions except that the scale is about one-third. It seems that, whatever are the causes of the change in quantum efficiency with alcohol concentration, the same factors operate in acid and neutral solution.

Discussion of Results.

The results for acid solutions seem to point to the conclusion that the true quantum efficiency of the photochemical process is

the decomposition of one dichromate ion and the oxidation of 3 molecules of alcohol per quantum absorbed. The measured quantum efficiency never reaches its true value because disturbing factors cause its diminution in mixtures containing excess of either alcohol or water. The diminution at high alcohol concentrations may be due to the appearance of a new substance, such as an alkyl chromate, since here the thermal reaction becomes very fast. If this is a correct deduction, it is improbable that the reaction really consists of the simultaneous collision of 3 alcohol molecules with an activated dichromate ion; and the simplest assumption is that the real photoactive substance is an alcoholated dichromate ion, *i.e.*, an ion with alcohol molecules attached by co-ordinate links. The diminution on the low alcohol concentration side would then be due to the equilibrium between non-photoactive hydrated dichromate ions and the photoactive alcoholated ions.

Applying the mass law as an approximation for the formation of a hydrate and an alcoholate, we have :

$$\frac{(Cr_2O_7)(H_2O)^n}{(Cr_2O_7,nH_2O)} = K_1; \quad \frac{(Cr_2O_7)(ROH)^m}{(Cr_2O_7,mROH)} = K_2.$$

Putting, for simplicity, $n = m$,

$$\frac{\text{Mol. fraction } H_2O}{\text{Mol. fraction ROH}} \times \sqrt[n]{\frac{\text{(alcoholate)}}{\text{(hydrate)}}} = K,$$

or roughly, at low alcohol concentrations :

$$\frac{\text{Mol. fraction } H_2O}{\text{Mol. fraction ROH}} \times \sqrt[n]{\text{Quantum efficiency}} = K.$$

The following calculations from the experimental data show that $n = 1$ approximately :

Methyl alcohol.

Alcohol, mols./l.	Mol. fraction $H_2O/ROH \times$ (quantum efficiency).
5·5	7·4
11	6·5
16	6·8
23	6·4
31	5·6

Ethyl alcohol.

Alcohol, mols./l.	Mol. fraction $H_2O/ROH \times$ (quantum efficiency).
3·3	14
7·1	20
11·4	21
16·9	23
23·6	18

n-Propyl alcohol.

Alcohol, mols./l.	Mol. fraction $H_2O/ROH \times$ (quantum efficiency).
3	25
4·5	29
9·5	35
14	28
19·4	24

*iso*Propyl alcohol.

Alcohol, mols./l.	Mol. fraction $H_2O/ROH \times$ (quantum efficiency).
4	26
9·2	43
19·4	27·6

In order to make the hypothesis fit the measurements, therefore, it must be assumed that only one molecule of alcohol or water is attached to each dichromate ion. It is hardly possible to accept this result, as it does not remove the difficulty of the oxidation of 3 molecules of alcohol per quantum absorbed.

An alternative hypothesis is that the activated dichromate ions have a mean "life" and only react if they collide with alcohol molecules during this "life." Applying an approximate equation (Grüss, *Z. Elektrochem.*, 1923, **29**, 144),

$$\text{Quantum efficiency} = 4\pi\sigma^2nct/3v,$$

where v = number of volumes of solution containing one volume of alcohol; n = number of molecules in 1 c.c.; $\sigma = 10^{-8}$ cm.; c = velocity of dichromate ion; t = "life" of activated dichromate ion.

It is significant from the point of view of this hypothesis that the quantum efficiency for all the alcohols is approximately halved at a dilution of 1 : 3; whence $t = 3 \times 10^{-11}$ second.

This time is of the order of that required for an electron shift in a molecule, and is much shorter than the life of the activated molecules of chlorine (Grüss, *loc. cit.*) and iodine (Briers, Chapman, and Walters, J., 1926, 562). The result is not improbable, because the long life of activated halogen molecules may represent the time of recombination of atoms formed after activation. No dissociation of this kind is to be expected with the dichromate ion. The mechanism of the reaction, however, must still be considered to be very imperfectly understood.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL AND TRINITY COLLEGES,
OXFORD.

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CCCXVII.—*Equilibrium in the Systems* $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°; *also in the System* $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

By ROBERT MARTIN CAVEN and WILLIAM JOHNSTON.

THE authors have previously shown (J., 1926, 2628), from an investigation of the system $MnSO_4$–K_2SO_4–H_2O at 25°, that at this temperature the double salt is tetrahydrated ($MnSO_4,K_2SO_4,4H_2O$). Since manganese sulphate itself crystallises with $4H_2O$ at 25°, and with $7H_2O$ at 0°, it was decided to investigate the hydration of its potassium double salt at 0°, in the expectation that it might

then be hexahydrated, and thus conform to the general type: $M''SO_4,M'_2SO_4,6H_2O$. Moreover, since manganese ammonium sulphate conforms to this general type, even at 25°, it was decided also to investigate the system $MnSO_4$–$(NH_4)_2SO_4$–H_2O at 0°, and thus to compare the kinds of isotherm obtained in the two cases. Further, this system was investigated at 25° by Schreinemakers (*Chem. Weekblad*, 1909, **6**, 131), and in the present paper his results are compared with those obtained by the authors (*loc. cit.*) for the system $MnSO_4$–K_2SO_4–H_2O at the same temperature.

Also, in order to study the influence of the water of crystallisation of the double salt on the type of isotherm obtained, it was decided to investigate the system $CuSO_4$–Na_2SO_4–H_2O at various temperatures, the double salt in this case always crystallising with $2H_2O$. This system has already been studied by several workers. Diacon (*Jahresber.*, 1866, 61) investigated it at 0°, and his results show that the double salt $CuSO_4,Na_2SO_4,2H_2O$ does not exist at this temperature in contact with solutions of its component salts. Nevertheless, the continuous increase in solubility of each of the two single salts caused by addition of the other salt up to the triple point indicates the presence of a considerable amount of the double salt or its ions in solution. Koppel (*Z. physikal. Chem.*, 1903, **42**, 1) showed that below 16·7° the double salt does not crystallise from a solution of its component salts; and from his results he drew a series of isotherms, showing an increased range of double salt formation above this temperature, which do not seem to be justified. Moreover, these hypothetical isotherms indicate that, from 0° to about 30°, whilst the solubility of sodium sulphate is increased by the addition of copper sulphate, that of copper sulphate is decreased by the addition of sodium sulphate. This conclusion contradicts Diacon's results at 0°. Massink investigated the same system at 20° (*Z. physikal. Chem.*, 1916, **92**, 351),* and showed a short range of double salt formation, with continuous increase of solubility of each of the single salts on addition of the other, up to the corresponding triple point. He gave, however, only one point within the double-salt range.

In view, therefore, of the conflicting and inadequate results of previous workers, the authors felt justified in investigating this system at 0° and 25°; and, since sodium sulphate is decahydrated below 33° and anhydrous above that temperature, they also decided to investigate the system above 33° (at 37·5°), to discover what

* According to an abstract of this paper (*Chem. Weekblad*, 1917, **14**, 756), Massink also investigated the system at 35°. Reference to the original paper shows that 35° is mentioned, but that the results supposed to be obtained at that temperature are missing.

influence the change in hydration of sodium sulphate had upon the isotherm.

EXPERIMENTAL.

The Systems $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°.

For the manganese–potassium system, solutions of the two salts were made at atmospheric temperature, and various proportions of these solutions were placed successively in a flask, fitted with a stirrer, and kept immersed in a mixture of ice and water. The mixtures were stirred for 3 days before portions of the solutions were separated and analysed. The manganese was estimated volumetrically by the Volhard method, the total sulphate determined, and the potassium sulphate calculated. The same procedure was carried out with the manganese–ammonium system, except that, as the solid phases are known, they were not analysed. The ammonia and total sulphate were determined.

In Table I, the results for the manganese–potassium system at 0° are expressed as g. per 100 g. of solution or of moist solid, and the triangular diagram is used to determine the composition of the double salt (Fig. 1). In Table II, the same results, and those for the manganese–ammonium system at 0°, are expressed as mols. per 1000 g. of water; and these results are then compared graphically by means of rectangular co-ordinates with those previously obtained by Schreinemakers and the authors at 25° (Figs. 2 and 3).

The System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

For this system at 0°, the procedure was as above, although only the liquid phases were analysed. Copper was estimated iodometrically, and total sulphate determined. For the systems at 25° and 37·5°, solutions of the two salts were made at temperatures about 15° above those required, and various proportions of the two solutions were placed in a flask, fitted with a stirrer, and kept in a thermostat at 25° ± 0·1° or 37·5° ± 0·1°. The solutions were stirred for 3 days before portions were separated and analysed. The results are expressed in Table III, and in Fig. 4 by means of rectangular co-ordinates, those of Diacon and Massink being also included in the same figure.

Conclusions.

Manganese Double Sulphates.—The following points arise:

1. Manganese potassium sulphate crystallises at 0°, as well as at 25°, with $4H_2O$.

2. Its isotherm at 0° resembles the corresponding isotherm at 25°, except that it shows a more rapid increase in solubility of

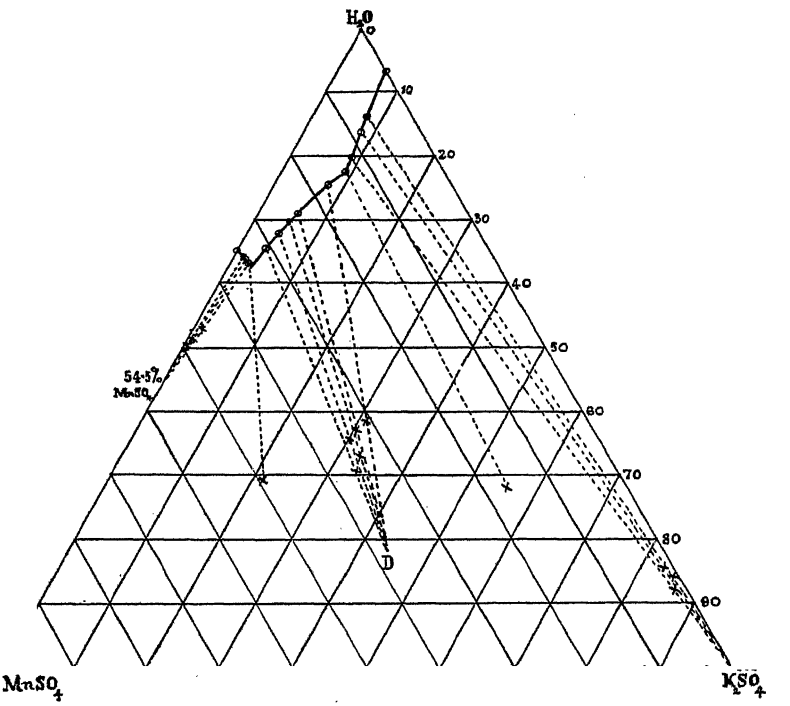
TABLE I.

The System $MnSO_4$–K_2SO_4–H_2O *at* 0°.

D.S. = Double salt.

Solutions.			Moist solids.			
K_2SO_4.	$MnSO_4$.	H_2O.	K_2SO_4.	$MnSO_4$.	H_2O.	Solid phase.
—	34·78	65·22	—	—	—	$MnSO_4,7H_2O$.
1·68	34·49	63·83	0·42	49·31	50·27	
1·85	34·53	63·62	0·70	48·00	51·30	
2·81	34·38	62·81	1·24	45·85	52·91	
3·35	34·30	62·35	21·52	49·49	28·99	$MnSO_4,7H_2O$ and D.S.
4·00	30·28	65·72	33·46	36·00	30·54	D.S. = $MnSO_4,K_2SO_4,4H_2O$.
4·48	27·62	67·90	30·31	34·46	35·23	
5·00	25·50	69·50	32·84	34·50	32·66	
5·54	23·64	70·82	30·46	32·98	36·56	
7·69	17·39	74·92	30·82	30·60	38·58	
8·88	13·68	77·44	55·60	16·90	27·50	D.S. and K_2SO_4.
8·48	11·80	79·72	86·00	1·82	12·18	K_2SO_4.
7·97	8·21	83·82	82·81	1·52	15·67	
7·75	6·21	86·04	84·55	1·11	14·34	
6·82	—	93·18	—	—	—	

FIG. 1.



Equilibrium diagram $MnSO_4$–K_2SO_4–H_2O *at* 0°.

The composition of the double salt is shown by the co-ordinates of the point D, *at which broken lines drawn through the "rests" intersect, to be* $MnSO_4,K_2SO_4,4H_2O$. *Broken lines drawn through rests for the single salts intersect at points showing* $MnSO_4,7H_2O$ (% $MnSO_4$ = 54·5) *and* K_2SO_4 (100%).

TABLE II.

The Systems $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°

(M = Manganese sulphate; K = Potassium sulphate; A = Ammonium sulphate; D = Double salt.)

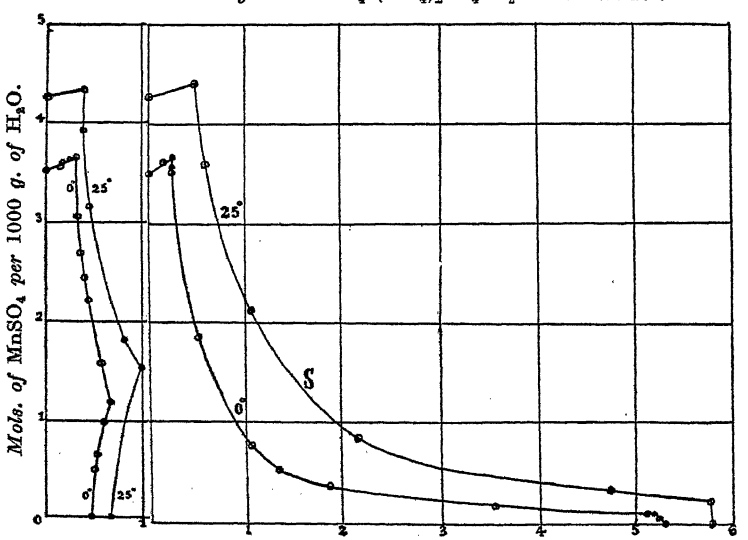
Mols. of K_2SO_4 per 1000 g. of H_2O.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Solid phase.	Mols. of $(NH_4)_2SO_4$ per 1000 g. of H_2O.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Solid phase.
—	3·533	M	—	3·533	M
0·151	3·580	M	0·168	3·623	M
0·167	3·594	M	0·251	3·665	M and D
0·257	3·624	M	0·260	3·565	D
0·308	3·642	M and D	0·261	3·525	D
0·349	3·051	D	0·531	1·868	D
0·379	2·698	D	1·069	0·769	D
0·413	2·430	D	1·315	0·531	D
0·447	2·211	D	1·864	0·377	D
0·589	1·537	D	3·551	0·167	D
0·659	1·169	D and K	3·993	0·138	D
0·611	0·978	K	5·135	0·075	D
0·546	0·649	K	5·229	0·081	D and A
0·517	0·478	K	5·254	0·017	A
0·420	—	K	5·327	—	A

FIG. 2.

A.

System $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0° *and* 25°.

FIG. 3.



B. *Mols. of* $(NH_4)_2SO_4$ *per* 1000 *g. of* H_2O.

S = *Curve drawn from results of Schreinemakers at* 25°.
Double salt is $MnSO_4,(NH_4)_2SO_4,6H_2O$ *at both temperatures.*

A.

System $MnSO_4$–K_2SO_4–H_2O *at* 0° *and* 25°.

B.

Mols. of K_2SO_4 *per* 1000 *g. of* H_2O.

Double salt is $MnSO_4,K_2SO_4,4H_2O$ *at both temperatures.*

TABLE III.

The System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

(D.S. = Double salt.)

Temperature : 0°.

Mols. per 1000 g. of H_2O.		
$CuSO_4$.	Na_2SO_4.	Solid phase.
—	0·387	$Na_2SO_4,10H_2O$.
0·213	0·415	
0·415	0·450	
0·590	0·468	
1·047	0·526	$Na_2SO_4,10H_2O$ + $CuSO_4,5H_2O$.
0·998	0·306	$CuSO_4,5H_2O$.
0·970	0·175	
0·929	—	

Temperature : 25°.

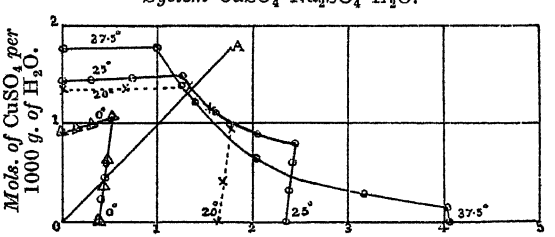
Mols. per 1000 g. of H_2O.		
$CuSO_4$.	Na_2SO_4.	Solid phase.
—	2·353	$Na_2SO_4,10H_2O$.
0·256	2·394	
0·593	2·432	
0·781	2·461	$Na_2SO_4,10H_2O$ + D.S.
0·847	2·057	D.S. = $CuSO_4,Na_2SO_4,2H_2O$.
0·979	1·717	
1·068	1·603	
1·457	1·323	$CuSO_4,5H_2O$.
1·449	0·765	
1·433	0·325	
1·428	—	

Temperature : 37·5°.

Mols. of $CuSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	4·066	Na_2SO_4.
0·162	4·046	Na_2SO_4 + D.S.
0·280	3·183	D.S. = $CuSO_4,Na_2SO_4,2H_2O$.
0·678	2·049	
0·821	1·800	
1·209	1·406	
1·402	1·242	
1·770	1·007	D.S. + $CuSO_4,5H_2O$.
1·754	—	$CuSO_4,5H_2O$.

FIG. 4.

System $CuSO_4$–Na_2SO_4–H_2O.



Diacon's results at 0° *are indicated thus* △.
Massink's ,, ,, 25° ,, ,, ,, ×, *and the isotherm by a broken line.*
OA *A line of equimolecular proportions to show solubility of double salt.*

manganese sulphate with addition of potassium sulphate up to the triple point. Some difference would be expected, since at 0° the solid phase is $MnSO_4,7H_2O$, whereas at 25° it is $MnSO_4,4H_2O$.

3. The 0°-isotherm of the potassium system differs greatly from that of the ammonium system, the range of double salt formation

in the case of the latter being much the greater. This is traceable to two factors: (*a*) the much greater solubility of ammonium sulphate, (*b*) the fact that the ammonium double salt crystallises with $6H_2O$, whereas the potassium double salt crystallises with $4H_2O$.

4. The 0°-isotherm of the ammonium system resembles the 25°-isotherm, as shown by Schreinemakers's results. Two points, however, should be noted: (*a*) The increase in solubility of manganese sulphate caused by ammonium sulphate at 25° is accentuated at 0° (compare the potassium system at 0° and 25°); (*b*) the decrease in solubility of ammonium sulphate caused by manganese sulphate at 25° is accentuated at 0°.

5. The isotherms for manganese ammonium sulphate, but not for the corresponding potassium salt, closely resemble those for the analogous copper salt (Caven and Mitchell, J., 1924, **125**, 1428).

Copper Sodium Sulphate.—A study of the results for the $CuSO_4$–Na_2SO_4–H_2O system shows a number of interesting points (see Fig. 4):

1. Diacon's results at 0° have been confirmed: there is no formation of double salt, but an increase in solubility of each single salt is caused by the presence of the other.

2. At 25°, the range of double salt formation is fairly wide. The addition of each component increases the solubility of the other up to the corresponding triple point where the double salt begins to crystallise. In the case of copper sulphate, this increase is slight but definite, in agreement with Massink's results, but in contradiction to those of Koppel.

3. At 37·5°, the range of double salt formation is greatly increased. It is to be noted, however, that although copper sulphate still shows a slight increase of solubility in presence of sodium sulphate, sodium sulphate now shows a decrease of solubility in presence of copper sulphate. A change in the form of the isotherm here is to be expected owing to the change of hydration of solid sodium sulphate.

4. The increase in range of double salt formation with rise of temperature is connected with some remarkable relationships seen when the isotherms of different temperatures are compared. Thus, although the solubilities of the single salts at 20° are less than at 25°, the double salt curve at 20°, according to Massink, appears to coincide through part of its course with the corresponding curve of the authors at 25°; and the double salt curve at 37·5°, according to the authors' results, actually falls within the corresponding curve at 25°, and even recedes from it at the sodium sulphate end because of the shortness of the solubility curve of sodium sulphate which has become anhydrous. It is evident, moreover, that the extent of the

double salt curve at 37·5° is connected with the greatly increased solubility of sodium sulphate at that temperature.

5. Thus it is concluded from the authors' results at 25° and 37·5° that the solubility of the double salt decreases with rise of temperature; and it may be supposed that the solubility at 20° is actually slightly greater than that at 25°, although Massink's result compared with the authors' does not show this.

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ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, August 6th*, 1927.]

CCCXVIII.—*Complex Metallic Ammines. Part IX. The Introduction of Nitrophenol Radicals into Cobaltammine Complexes. Distinctive Behaviour of Mononitrophenoxides.*

By JAMES COOPER DUFF and EDWIN JOHN BILLS.

IN Part VIII (J., 1923, **123**, 561) it was shown that sodium salts of carboxylic acids react with aquopentamminocobaltic nitrate to give acidopentamminocobaltic salts. The sodium derivatives of several nitrophenols have now been found to react similarly with aquopentamminocobaltic nitrate and with bisaquobisethylenediamminocobaltic salts. Mono-, di-, and tri-nitrophenols have been used to examine as far as possible the influence of the number and the orientations of the nitro-groups. The unexpectedly varying nature of the series of compounds obtained is discussed below.

Previously the only nitrophenol which had been found to give cobaltammine derivatives was picric acid. Morgan and King (J., 1922, **121**, 1723) have described the reactions which occur between several cobaltammine salts and certain nitro-dyes. They found that sodium picrate reacts with aquopentamminocobaltic chloride to give aquopentamminocobaltic picrate, and suggested that nitro-dyes such as picric acid and dinitronaphthol do not, in their reactions with cobaltammines, become implicated in the cobalt complex, thus differing noticeably from the *o*-quinoneoxime (nitrosonaphthol) dyes examined similarly by Morgan and Smith (J., 1921, **119**, 704). The latter found that the quinoneoxime radical, although univalent as regards principal valency, functions as a chelate group in the complex, being linked to cobalt through a principal valency (electro-valency) and a residual valency (co-

valency). Morgan and King further suggest (*loc. cit.*) that the lack of residual valency shown by the picrate radical may be taken as evidence corroborating its *p*-quinonoid structure. In no case did they find that the picrate radical became part of the cobalt complex. It has now been found that nitrophenoxide radicals can be induced to form part of the complex, particularly in the tetrammine type. In most cases, the nitrophenoxide radicals were linked through a principal valency, but two outstanding examples have been obtained in which a complete molecule of nitrophenol appears to be implicated in the complex through residual valency.

The mononitrophenoxides have yielded results which indicate a structural difference between *m*-nitrophenol and the *o*- and *p*-isomerides, the quinone structure probably applying to the last two but not to the first. The evidence supports the views of Hantzsch (*Ber.*, 1907, **40**, 330) and of Hewitt, Johnson, and Pope (J., 1913, **103**, 1626) on these compounds.

Conductivity measurements have been used in the present work as the best method available for determining whether a nitrophenoxide radical is within the complex ion or not. It was recorded in Part VIII (*loc. cit.*) that during conductivity measurements with dilute solutions, the platinum-black of the electrodes was capable in the case of compounds of the type $[Co(NH_3)_5X]NO_3$ (X = a dibasic acid radical) of causing internal hydrolysis, changing the acido-salt into an aquo-salt. Examples of this effect have again been encountered (see Experimental), although the compounds concerned are different in type from those in Part VIII. There has also been found in the case of a *p*-nitrophenol derivative (p. 2373) an example where the platinum-black apparently induces the displacement of water from the complex by a nitrophenoxide radical. This is the only case where a fall in the value for μ has been found to occur as the result of the catalytic influence of platinum-black. It should be noted that neither type of change due to the platinum-black requires any current to be passing between the electrodes. As a further check on the value of the conductivity figures those of the corresponding sodium nitrophenoxides are given at the end of this paper.

The Pentammine Compounds.

Sodium mono- and di-nitrophenoxides form alkaline aqueous solutions which complicate the reactions with aquopentamminocobaltic nitrate. In each case there was liberation of nitrophenol and no cobaltammine compound containing *o*- or *m*-nitrophenol could be separated. The reaction in these two cases was nearly quantitatively that of the equation $[Co(NH_3)_5,H_2O](NO_3)_3 + NaO\cdot C_6H_4\cdot NO_2 = [Co(NH_3)_5(OH)](NO_3)_2 + NaNO_3 + HO\cdot C_6H_4\cdot NO_2$.

Sodium *p*-nitrophenoxide, in addition to yielding some free *p*-nitrophenol, gave a fair yield of p-*nitrophenoxopentamminocobaltic* p-*nitrophenoxide* [I; X = *p*-$C_6H_4(NO_2)\cdot O\cdot$].

$[Co(NH_3)_5X]X_2$ (I.) $\quad [Co(NH_3)_5,H_2O]X_3$ (II.) $\quad \left[Co(NH_3)_5X\right]\begin{matrix}X\\OH\end{matrix}$ (III.)

It is of interest that of the three nitrophenols only the *p*-isomeride is capable of combining with the corresponding sodium derivative; this may account for the subsequent production of a pentammino-derivative in this case, and explain the lack of success with *o*- and *m*-nitrophenols. By using the double compound of sodium *p*-nitrophenoxide and *p*-nitrophenol, a better yield of the compound (I) is obtained.

The sodium derivatives of 2 : 4- and 2 : 6-dinitrophenols gave simple aquopentammino-salts [II; X = $C_6H_3(NO_2)_2\cdot O\cdot$]. Sodium picrate yielded *picratopentamminocobaltic picrate* [I; X = $C_6H_2(NO_2)_3\cdot O\cdot$]; its relation to the aquo-picrate prepared by Morgan and King (*loc. cit.*) is considered in the experimental part. When picric acid reacts with carbonatopentamminocobaltic nitrate, two compounds can be obtained. If the carbonato-salt is used in excess, there is produced a basic salt (III), otherwise the normal compound (I) is again obtained.

The two compounds of special interest in this section are those of *p*-nitrophenol and of picric acid (III). Both these undergo a change of conductivity in the Kohlrausch cell with platinised electrodes at the ordinary temperature; this only ceases when an aquo-salt has resulted in each case:

$$[Co(NH_3)_5X]X_2 + H_2O \longrightarrow [Co(NH_3)_5,H_2O]X_3$$

Thus for the *p*-nitrophenol compound μ (for $v = 1024$) changes from 177·7 to 322·5 in 24 hours, accompanied by a colour change, while the stock solution shows but little hydrolysis after 3 months in a stoppered flask. The solutions which have been catalytically hydrolysed in the cell remain permanently hydrolysed.

The Bisethylenediammine Compounds.

The sodium derivatives of all the nitrophenols examined react with bisaquobisethylenediamminocobaltic bromide to give crystalline compounds containing nitrophenol groups. The resulting compounds showed unusual differences. Sodium picrate gave *aquopicratobisethylenediamminocobaltic picrate* (IV; X = picrate radical) and sodium 2 : 4-dinitrophenoxide gave a similar compound (as IV),

whilst the 2 : 6-isomeride yielded a basic salt (V; X = 2 : 6-dinitrophenoxide radical).

(IV.) $\left[\begin{matrix}H_2O\\X\end{matrix}Co\,en_2\right]X_2$ $\left[\begin{matrix}H_2O\\X\end{matrix}Co\,en_2\right]\begin{matrix}OH\\X\end{matrix}$ (V.)

The outstanding results in this section were obtained from the mononitrophenoxides. One circumstance common to all three isomerides was that the resulting cobaltammine compounds contained a molecule of nitrophenol in addition to three nitrophenoxide radicals. The manner in which this nitrophenol molecule occurs in the compound is different in each case. Sodium *m*-nitrophenoxide produced a molecular compound between *bis*-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* and *m*-nitrophenol (VI; X = *m*-nitrophenoxide radical), in which the latter molecule is outside the complex.

(VI.) $[Co\,en_2\,X_2]X,HX$ $\left[\begin{matrix}X\\HX\end{matrix}Co\,en_2\right]X_2$ (VII.)

From sodium *o*- and *p*-nitrophenoxides it was possible to obtain *nitrophenolnitrophenoxobisethylenediamminocobaltic nitrophenoxide* (VII; X = *o*- or *p*-nitrophenoxide radical). This is a new type of compound because the complete molecule of *o*- or *p*-nitrophenol is linked by residual valency (co-valency) in the same manner as a molecule of water in the case of aquocobaltammine salts. Formula (VII) is supported by the facts that (1) unlike all other compounds in this series, the aqueous solutions of the two salts concerned can be acidified without discharging the yellow or red colour, respectively, of the *p*- or *o*-nitrophenol compound, and (2) the aqueous solutions of these two salts when heated and then cooled and acidified have their colour discharged, yet the heating has caused no change in the values for molecular conductivity. This means that the substances hydrolyse in hot solutions, but only to the extent of having the molecule of nitrophenol displaced by a molecule of water, as in (IX) :

(VIII.) $\begin{matrix}[XCo\,en_2]\,X_2\\ O{=}C_6H_4{=}NO_2H\end{matrix} + H_2O \longrightarrow \left[\begin{matrix}X\\H_2O\end{matrix}Co\,en_2\right]X_2,HX.$ (IX.)

Since the molecule of nitrophenol in the complex is apparently concerned in the colour of the cold acid solution, it would appear reasonable to attribute to this complete nitrophenol molecule in the complex the corresponding *o*- or *p*-quinonoid structure (VIII), especially as the red and yellow colours of the respective compounds correspond to those of *o*- and *p*-quinones. An important point in this connexion is the fact that no free *o*-, *m*-, or *p*-nitrophenol was present at the beginning of the preparation of these compounds. The nitrophenol was liberated in each case during the reaction

between the sodium derivative and the bisaquocobaltammine salt, the probable reaction being as follows :

$$[\mathrm{Co\,en_2\,(H_2O)_2}]\mathrm{Br_3} + \mathrm{NaO{\cdot}C_6H_4{\cdot}NO_2} \longrightarrow \left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{HO}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_2} + \mathrm{NaBr} + \mathrm{HO{\cdot}C_6H_4{\cdot}NO_2}.$$

The foregoing results suggest that whilst sodium *m*-nitrophenoxide is not quinonoid in structure, yet the *o*- and *p*-nitrophenoxides probably are; and further, when these are decomposed as in the above equation, the newly-liberated nitrophenol has the quinonoid structure and is linked up in this form in the complex in place of water.

Whilst only one cobaltammine compound of this series could be isolated from each of the *o*- and *m*-nitrophenoxides, the *p*-nitrophenoxide was found capable of producing three others in addition to (VII); by use of its addition compound with *p*-nitrophenol, $\mathrm{NaC_6H_4O_3N,C_6H_5O_3N,2H_2O}$, two compounds represented by (IV) and (IX) were obtained by varying the conditions of reaction. In dilute aqueous solution, particularly in the presence of platinum-black, both these compounds undergo change, a nitrophenoxide radical entering the complex and displacing water :

$$\left[\begin{matrix}\mathrm{X}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{X_2,HX} \longrightarrow [\mathrm{Co\,en_2\,X_2}]\mathrm{X,HX} + \mathrm{H_2O}.$$

On attempting to recrystallise compound (IX) from hot water, some nitrophenol is liberated, yet from the solution it is possible to obtain crystals of the molecular compound *bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide*–p-*nitrophenol* (as VI), corresponding to that obtained from *m*-nitrophenol.

Experimental.

Electrical Conductivity Measurements.—The method of measurement recorded in Part VII (J., 1922, **121**, 453) was adopted. Since most of the compounds were only moderately soluble, measurements were limited to $v = 1024$ and 2048 at 25°, at which temperature all determinations were made. Fresh solutions were made for each. The Kohlrausch cell constant was 0·2117 and the resistances measured did not greatly exceed 5000 ohms. Where conductivity changes due to the platinised electrodes were found, these were checked on new solutions. To find the extent to which change occurred it was usually necessary to leave the cell solution and the stock solution for 24 hours in the thermostat and then redetermine μ for each. No attempt was made to compare the rates at which changes occurred, as it was noted that these only took place in the neighbourhood of the electrodes. Samples of solutions which had

undergone change in this way were kept in closed tubes for 3 months and again examined. In no case had there been any tendency to revert to the original form. With unplatinised electrodes practically no catalytic effect was noticeable.

The Pentammine Series.

The Cobaltammine Reagent.—5 G. of carbonatopentamminocobaltic nitrate, 30 c.c. of water, and 20 c.c. of 2*N*-nitric acid were maintained at 45° until effervescence ceased. The solution was neutralised with 2*N*-sodium hydroxide. For the following compounds, this reagent was mixed at 45° with a solution of the corresponding sodium derivative (3 mols.) in the minimum amount of water. Except in the case of the picrate it was necessary to extract the washed precipitate with alcohol and ether to remove free nitrophenol or dinitrophenol. The product was then crystallised from water at 65°.

Sodium *o*- and *m*-nitrophenoxides produced only a precipitate of free nitrophenol. On addition of sufficient alcohol to retain this in solution, long red needles slowly separated; these were identified by analysis and reactions as hydroxopentamminocobaltic nitrate (see equation, p. 2366).

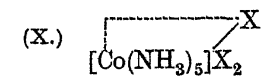
The following compounds are all easily decomposed by dilute acid or alkali. In the crystalline form and in solution, they begin to decompose at 70—80°.

p-*Nitrophenoxopentamminocobaltic* p-*nitrophenoxide* (as I; with $3H_2O$) was obtained in minute, orange, oblong plates (Found: Co, 9·34; NH_3, 13·76; nitrophenoxide, 67·8; H_2O, 8·21. $C_{18}H_{27}O_9N_8Co,3H_2O$ requires Co, 9·64; NH_3, 13·88; nitrophenoxide, 67·64; H_2O, 8·82%). By the use of the addition compound of sodium *p*-nitrophenoxide and *p*-nitrophenol, the same compound was obtained in better yield (Found: Co, 9·24; nitrophenoxide, 65·77%); $\mu_{1024} = 177{\cdot}7$ and $\mu_{2048} = 189{\cdot}2$; 24 hours later the cell solution had $\mu_{1024} = 322{\cdot}5$ and $\mu_{2048} = 322{\cdot}2$, whilst the stock solution had $\mu_{1024} = 181{\cdot}2$ and $\mu_{2048} = 189{\cdot}4$. The cell solution had become greenish-yellow, whilst the flask solution remained golden-yellow. The solutions were kept sealed for 3 months, and the two cell solutions then had $\mu_{1024} = 340{\cdot}5$ and $\mu_{2048} = 342{\cdot}8$, and the stock solutions $\mu_{1024} = 208{\cdot}4$ and $\mu_{2048} = 245{\cdot}3$. A few minutes in the cell caused a greater change than 3 months in the stock flask.

Aquopentamminocobaltic 2 : 4-*dinitrophenoxide* (as II; with $3H_2O$) was obtained as an orange, sandy, crystalline powder (Found: Co, 7·72; NH_3, 11·11; dinitrophenoxide, 71·88; H_2O, 8·86. $C_{18}H_{26}O_{16}N_{11}Co,3H_2O$ requires Co, 7·71; NH_3, 11·11; dinitrophenoxide, 71·76; H_2O, 9·41%); $\mu_{1024} = 284$ and $\mu_{2048} = 291{\cdot}6$.

Aquopentamminocobaltic 2 : 6-*dinitrophenoxide* (as II) was obtained as an orange-red, microcrystalline powder, only sparingly soluble in water (Found : Co, 8·29; NH_3, 12·20; dinitrophenoxide, 77·68. $C_{18}H_{26}O_{16}N_{11}Co$ requires Co, 8·29; NH_3, 11·95; dinitrophenoxide, 77·21%); $\mu_{2048} = 318{\cdot}4$.

Picratopentamminocobaltic picrate (as I; with $3H_2O$) was obtained in glistening, golden leaflets (Found : Co, 6·53; NH_3, 9·53; picrate, 78·2; H_2O, 6·91. $C_{18}H_{21}O_{21}N_{14}Co,3H_2O$ requires Co, 6·68; NH_3, 9·63; picrate, 77·55; H_2O, 6·12%). The same compound resulted from the reaction between picric acid (3 mols.) and carbonatopentamminocobaltic nitrate (Found : Co, 6·35; NH_3, 9·28; picrate, 76·8%). For conductivity measurements it was difficult to obtain a solution for $v = 2048$ without heating to 60°, and this apparently caused some hydrolysis. At 25°, $\mu_{2048} = 304$, changing in the cell in 2 days to 359·1. In view of this somewhat high value for an acidopentammine salt, the compound described by Morgan and King (*loc. cit.*) was prepared and examined : at 25°, $\mu_{2048} = 288$, changing in 3 hours in the cell to 360, and over-night to 415·3, whilst the stock solution only changed to $\mu_{2048} = 299$; it was noticed that the cell solution had changed from golden-yellow to greenish-yellow. These changes suggest that Morgan and King's compound $[Co(NH_3)_5H_2O]X_3$ is not simply an aquopentammine salt, as they assert. The molecule contains $2H_2O$ less than our compound and differs in appearance, but it can be changed to our picrato-salt by crystallisation from a hot dilute solution of picric acid. A possible explanation may be that in the compound of Morgan and King one of the picrate radicals is linked to the cobalt by residual valency and to the complex by principal valency as in (X). This could account

(X.) 

for the conductivity changes and the conversion by means of picric acid into our compound.

Picratopentamminocobaltic hydroxypicrate (III; with $2H_2O$) was obtained as a brown, microcrystalline powder by stirring powdered picric acid (1 mol.) into a concentrated solution of carbonatopentamminocobaltic nitrate at 60°. The product was recrystallised from water at 60° (Found : Co, 9·09; NH_3, 13·14; picrate, 69·85; H_2O, 5·18. $C_{12}H_{20}O_{15}N_{11}Co,2H_2O$ requires Co, 9·03; NH_3, 13·02; picrate, 69·83; H_2O, 5·51%); $\mu_{2048} = 203{\cdot}3$, changing in the cell in 12 hours to 352·2, while the stock solution remained at 203·3. The cell solution changed in colour from orange to greenish-yellow. After 3 months in a sealed tube, this solution gave $\mu_{2048} = 360$, whilst the stock solution gave 225·6. When the basic picrate was

dissolved in hot dilute picric acid solution, the normal picrato-salt separated on cooling.

Bisethylenediammine Series.

The Cobaltammine Reagent.—5 G. of carbonatobisethylenediamminocobaltic bromide, 30 c.c. of water, and 20 c.c. of 2*N*-nitric acid were maintained at 50° until effervescence ceased. The solution was neutralised with 2*N*-sodium hydroxide. It was freshly made for each of the following preparations.

o-*Nitrophenol*-o-*nitrophenoxobisethylenediamminocobaltic* o-*nitrophenoxide* (as VII; with $1H_2O$) was prepared by mixing the cobaltammine reagent at 50° with 7·5 g. of sodium *o*-nitrophenoxide (3 mols.) in 70 c.c. of water. After alcohol and ether extraction, the product was crystallised from water at 70°, yielding dark red, minute, glistening plates (Found: Co, 7·83; nitrophenoxide, 73·34. $C_{28}H_{33}O_{12}N_8Co,H_2O$ requires Co, 7·86; nitrophenoxide, 73·60%). The aqueous solution is red and changes to a more scarlet tint on addition of dilute mineral acids, with separation of some nitrophenol. The acid solution becomes faintly pink on boiling. A fresh aqueous solution of the compound becomes yellow when immersed in boiling water, and subsequent addition of acid gives only the pink colour of aquocobaltammine inorganic salts. It is inferred from these reactions that a complete molecule of *o*-nitrophenol is within the complex and is only readily replaced by a molecule of water in hot solutions. Dilute alkali causes complete hydrolysis immediately. The compound is appreciably soluble in alcohol and in acetone, but not sufficiently soluble to serve for an accurate estimation of the molecular weight: values obtained ebullioscopically ranged from 780 to 900. $\mu_{1024} = 135{\cdot}6$ and $\mu_{2048} = 142{\cdot}2$. After the latter solution had been heated on the water-bath to change the colour from red to yellow, μ_{2048} became 140·2.

Bis-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* + m-*nitrophenol* (as VI; with $1H_2O$) was obtained when the cobaltammine reagent at 50° was mixed with 7·5 g. of sodium *m*-nitrophenoxide in 70 c.c. of water. The mixture was filtered at 25° and the solution left over-night. The desired compound was obtained in brownish-red nodules (Found: Co, 7·81; nitrophenoxide, 72·98. $C_{28}H_{33}O_{12}N_8Co,H_2O$ requires Co, 7·86; nitrophenoxide, 73·6%). The aqueous solution is yellow and addition of dilute acid renders it pink, with liberation of all the nitrophenol; $\mu_{1024} = 75{\cdot}7$ and $\mu_{2048} = 71{\cdot}5$. The former value is high because of hydrolysis during the preparation of the solution. After this solution had been heated on the water-bath for 30 minutes, μ_{1024} became 101·5.

p-Nitrophenol was found capable of yielding the compounds A, B, C, D, as follows.

A. p-*Nitrophenol*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (as VII; with $3H_2O$). To obtain this compound it was necessary to use a solution of sodium *p*-nitrophenoxide freshly prepared from the nitrophenol: the use of the crystallised salt resulted in a mixture of A and C. The cobaltammine reagent at 50° was mixed with a solution of 6·5 g. of *p*-nitrophenol in 46·8 c.c. of *N*-sodium hydroxide and 40 c.c. of water. The precipitate, washed with alcohol and ether to remove *p*-nitrophenol, was crystallised from water at 70°. In this way, A was obtained in dark brown microcrystals which assumed a purple shade on dehydration at 90° (Found: Co, 7·30; nitrophenoxide, 69·45; H_2O, 6·72. $C_{28}H_{33}O_{12}N_8Co,3H_2O$ requires Co, 7·50; nitrophenoxide, 70·23; H_2O, 6·87%). The compound is appreciably soluble in alcohol and acetone. The aqueous solution is orange and when acidified retains a yellow colour for several minutes. If the solution is heated, then cooled and acidified, it becomes pink immediately. $\mu_{1024} = 130·2$ and $\mu_{2048} = 139·6$. After the latter solution had been heated for 15 minutes at 90° it had $\mu_{2048} = 125·7$, changing in the cell to 91·0 after 24 hours and 78·8 after 48 hours. This indicates a change from A through C into D (p. 2374). The hydrated salt changes slowly in the solid state, passing into the compound C, since after 4 months it gave aqueous solutions which at once became pink on being acidified. The anhydrous form of the salt is more stable.

B. *Aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (as IV; with $2H_2O$) was obtained as a light brown, crystalline powder when the cobaltammine reagent was mixed at 70° with 15 g. of the double compound of sodium *p*-nitrophenoxide and *p*-nitrophenol in 200 c.c. of water. The precipitate was filtered immediately and free nitrophenol removed by ether extraction (Found: Co, 9·14; nitrophenoxide, 63·83. $C_{22}H_{30}O_{10}N_7Co,2H_2O$ requires Co, 9·11; nitrophenoxide, 63·98%). An aqueous solution is immediately decomposed by dilute acid, a distinction from A. On heating to 80°, the aqueous solution decomposes with separation of *p*-nitrophenol, yet the impure crystals which separate on cooling contain more than three equivalents of nitrophenoxide. There is evidently a tendency for B to pass into the more stable compound C. $\mu_{1024} = 115·8$ and $\mu_{2048} = 122·8$; the latter changes in the cell to 84·3.

C. *Aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (as IX; with $1H_2O$) was obtained in orange-brown microcrystals by mixing the cobaltammine reagent with 15 g. of the double sodium salt in 200 c.c. of water at 40°, filtering the solution after 2 hours, and removing free *p*-nitrophenol by ether

extraction (Found: Co, 7·74; nitrophenoxide, 71·34; H_2O, 3·8. $C_{28}H_{35}O_{13}N_8Co,H_2O$ requires Co, 7·68; nitrophenoxide, 71·87; H_2O, 4·68%). In solution, C behaves similarly to B. $\mu_{1024} = 119·5$ and $\mu_{2048} = 118·8$; after 24 hours in the cell $\mu_{2048} = 70·1$ while the stock solution gave $\mu_{2048} = 117·9$. The results support the change of C into D as below.

D. *Bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (as VI; with $2H_2O$) was obtained from C above by crystallising it from water at 70°, filtering the solution from liberated *p*-nitrophenol, and leaving it over-night; the salt separated in dark brown nodules (Found: Co, 7·73; nitrophenoxide, 71·9; H_2O, 5·23. $C_{28}H_{33}O_{12}N_8Co,2H_2O$ requires Co, 7·68; nitrophenoxide, 71·87; H_2O, 4·68%). The yellow colour of the aqueous solution is changed to pink immediately by dilute acid. $\mu_{1024} = 88·0$ and $\mu_{2048} = 70·1$; the high value for μ_{1024} is due to the fact that the solution had been prepared at 40°.

Aquo-2 : 4-*dinitrophenoxobisethylenediamminocobaltic* 2 : 4-*dinitrophenoxide* (as IV; with $1H_2O$) was prepared by mixing the cobaltammine reagent at 60° with 9·6 g. of sodium 2 : 4-dinitrophenoxide (3 mols.) in 200 c.c. of water. After being washed, finally with ether, the pure compound crystallised from water at 70° in orange-red microcrystals (Found: Co, 7·71; dinitrophenoxide, 70·55; H_2O, 4·13. $C_{22}H_{27}O_{16}N_{10}Co,H_2O$ requires Co, 7·72; dinitrophenoxide, 71·86; H_2O, 4·71%); $\mu_{2048} = 184·1$—it was necessary to warm to 60° to obtain this solution.

Aquo-2 : 6-*dinitrophenoxobisethylenediamminocobaltic hydroxy*-2 : 6-*dinitrophenoxide* (as V) was obtained in brown microcrystals by the analogous method (Found: Co, 10·02; dinitrophenoxide, 63·45. $C_{16}H_{25}O_{12}N_8Co$ requires Co, 10·17; dinitrophenoxide, 63·10%); $\mu_{2048} = 165·7$.

Aquopicratobisethylenediamminocobaltic picrate (IV; with $4H_2O$) was obtained in orange, flat needles from the cobaltammine reagent and 12 g. of sodium picrate in 200 c.c. of water by the method used for the two preceding compounds (Found: Co, 6·16; picrate, 72·7; H_2O, 9·69. $C_{22}H_{24}O_{22}N_{13}Co,4H_2O$ requires Co, 6·18; picrate, 71·77; H_2O, 9·44%). The same compound was produced by the action of excess of picric acid in solution on carbonatobisethylenediamminocobaltic bromide at 60° (Found: Co, 6·32; picrate, 70·84%); $\mu_{2048} = 251·7$, without change in the cell on standing.

Analysis.—In both series cobalt was determined directly as sulphate by heating the compounds with concentrated sulphuric acid. The nitrophenols were estimated by heating with excess of titanous chloride solution and titrating the excess with standard ferric alum solution: in the pentammine series this was done after

precipitation of cobalt with sodium hydroxide, but in the bisethylenediammine series it was necessary to let the titanous chloride reduce both the cobaltic complex and the nitrophenol and subsequently to allow for the cobalt present. No estimation of ethylenediamine was made, since all the compounds in this series were found to yield the green *trans*-dichlorobisethylenediamminocobaltic chloride on evaporation with hydrochloric acid.

As standards for the conductivity values, the following values were determined (at 25°) for the various sodium derivatives of the nitrophenols :

	μ_{1024}.	μ_{2048}.
Sodium *o*-nitrophenoxide	82·0	92·9
Sodium *m*-nitrophenoxide	82·35	92·6
Sodium *p*-nitrophenoxide	86·35	90·0
Sodium 2 : 4-dinitrophenoxide	82·6	90·6
Sodium picrate	82·6	91·6

CENTRAL TECHNICAL COLLEGE,
BIRMINGHAM.

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CCCXIX.—*The Preparation of some Nitrohydroxybenzaldehydes and the Colour Relationships of their Substituted Phenylhydrazones.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

MONONITRO-*m*-HYDROXYBENZALDEHYDES were first described by Tiemann and Ludwig (*Ber.*, 1882, **15**, 2043) but correctly oriented by Friedländer and Schenck (*Ber.*, 1914, **47**, 3040), whilst Friedländer and Schreiber (*Ber.*, 1895, **28**, 1382) described the mononitration of *m*-methoxybenzaldehyde, thereby completing previous work by Ulrich (*Ber.*, 1885, **18**, 2571) and Rieche (*Ber.*, 1889, **22**, 2349). Tiemann and Ludwig's α- and β-dinitro-*m*-methoxybenzaldehydes, m. p.'s 155° and 110°, respectively, have not, however, been oriented; this problem, together with an investigation on the di- and trinitro-*m*-hydroxy- and the dinitro-*p*-hydroxy-benzaldehydes, is now dealt with.

Controlled direct dinitration of *m*-hydroxybenzaldehyde proved impracticable, the reaction products containing unchanged material and inseparable mixtures of nitro-compounds. Nitration of 6-nitro-3-hydroxybenzaldehyde gave two dinitro-products, m. p.'s 94° and 106°, whereas nitration of 2- and 4-nitro-3-hydroxybenzaldehydes gave single products melting at 94° and 106°, respectively, which must therefore be the 2 : 6- and 4 : 6-*dinitro-3-hydroxybenzaldehydes*. These could not be methylated by the ordinary methods, but a mixture of 2 : 6- and 4 : 6-*dinitro-3-methoxybenz-*

aldehydes was obtained by the dinitration of *m*-methoxybenzaldehyde at a lower temperature than that employed by Tiemann and Ludwig (*loc. cit.*), and separated by fractional crystallisation from hot benzene, in which the latter is five times more soluble than the former. Confirmation of their constitutions was obtained by nitration of the 6-, 4-, and 2-nitro-3-methoxybenzaldehydes, the first giving a mixture of two products, m. p.'s 157° and 131°, and the other two giving single products, of m. p.'s 131° and 157°, which are therefore 4 : 6- and 2 : 6-dinitro-3-methoxybenzaldehyde, respectively. Tiemann's α-compound (*loc. cit.*) is consequently the 2 : 6-dinitro-isomeride, whereas his β-compound is a mixture of this with the 4 : 6-isomeride.

All three mononitro- and both dinitro-3-hydroxybenzaldehydes give the same trinitrated product, which must therefore be the 2 : 4 : 6-*trinitro-3-hydroxybenzaldehyde*.

Nitration of 3-nitro-4-hydroxybenzaldehyde with pure nitric acid gives 3 : 5-*dinitro-4-hydroxybenzaldehyde*, but if sulphuric acid is present only picric acid is formed. It is noteworthy that the introduction of two nitro-groups into either *m*- or *p*-hydroxybenzaldehyde or their chloro-derivatives (Hodgson and Beard, J., 1926, 2030) gives products which all melt between 90° and 110°.

The facility of decomposition of the *p*-nitrophenylhydrazones of the various nitrohydroxybenzaldehydes appears to depend upon the positions of the nitro-groups in the aldehyde residue, *e.g.*, 2 : 6-dinitro-3-hydroxy- and -3-methoxybenzaldehyde-*p*-nitrophenylhydrazones explode at about 240° and 260°, respectively, whereas the 4 : 6-dinitro-isomerides are stable above 300°.

Colours and Colour-reactions.

The colours of the nitro- and *p*-bromo-phenylhydrazones of the above aldehydes, both as solids and in aqueous and alcoholic alkaline solution, are discussed in relation to positional influences.

Acidic groups in both *o*-positions to the aldehyde radical reduce the depth of colour of the solid phenylhydrazones in a similar way to that found by Chattaway and Clemo (J., 1923, **123**, 3041) for the hydrazine nucleus; thus, the phenylhydrazones of 2- and 3-nitrobenzaldehydes are respectively crimson and deep bright orange, whereas those of the corresponding dichloro-derivatives (2 : 5-dichloro-6-nitro- and -3-nitro-benzaldehydes) are orange-yellow and orange; the introduction of a *p*-nitro-group into the hydrazine nucleus causes a further reduction of colour, *e.g.*, to a pale yellow in the case of 2 : 5-dichloro-6-nitrobenzaldehyde-*p*-nitrophenylhydrazone.

The presence of the hydroxyl group modifies Chattaway and

Clemo's generalisation, for the *p*-nitrophenylhydrazone of 2-nitro-3-hydroxybenzaldehyde is much darker than that of the 6-nitro-isomeride, although the nitro-group is ortho in each case; methylation of the hydroxyl group, however, removes the disturbing effect, the *p*-bromophenylhydrazones of 2-nitro-3-hydroxy- and -3-methoxybenzaldehydes being deep nigre-brown and bright orange, respectively.

Alcoholic solutions of the hydrazones now described obey Chattaway and Clemo's generalisation. The exceptional case quoted by them—the phenylhydrazone of 2 : 5-dichloro-6-nitrobenzaldehyde—is not repeated, however, in the *p*-nitrophenylhydrazone of this aldehyde, which, instead of merely affording the magenta colour characteristic of substituted phenylhydrazones, as would be expected if the exceptional character persisted, now gives a pronounced blue colour, showing that the nitro-group in the aldehyde residue is again functioning in a quinonoid structure.

2 : 5-Dichloro-3-nitrobenzaldehydephenylhydrazone gives the pronounced brown colour with alkalis associated with Chattaway and Clemo's scheme, but the *p*-nitrophenylhydrazone gives a blue and not a magenta colour as expected.

The magenta colours given by *m*-hydroxy- and nitro-*m*-hydroxybenzaldehyde-*p*-nitrophenylhydrazones persist to much greater dilutions than if the hydroxyl group is absent, and that these colours are not due to salt formation alone is shown by the fact that the *m*-nitrophenylhydrazone of the *m*-hydroxyaldehyde gives no colour reaction.

The *p*-bromophenylhydrazones of the nitrohydroxyaldehydes are colourless in aqueous alkaline solution, thus, by contrast with the foregoing, showing that the methine group is far more resistant to quinonoid formation than the imino-group. This same difference is also illustrated by the fact that when aqueous alkaline solutions of benzaldehyde-*p*-nitrophenylhydrazone and *p*-nitrobenzaldehyde-phenylhydrazone are diluted, the colour of the former persists to much greater dilutions (about 400-fold). Differential suppression of colour is shown by the sequence of colour changes (blue, violet, magenta) on dilution of *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone.

The pronounced colour effects in alcoholic alkaline solutions when a nitro-group is in the para-position in each nucleus suggest a double quinonoid structure (*e.g.*, $OK\cdot NO{:}C_6H_4{:}C{:}N\cdot N{:}C_6H_4{:}NO\cdot OK$), since in a mixture of two singly-quinonoid compounds the magenta of the hydrazine-quinonoid compound would predominate, as it does if a *m*-hydroxyl group is present in the aldehyde nucleus.

Correction.—Hodgson and Beard (J., 1926, 2034) nitrated what was thought to be pure 4-chloro-3-hydroxybenzaldehyde and

obtained what they regarded as the 2- and 6-nitro-derivatives. It is now found that the 4-nitro-3-hydroxybenzaldehyde from which the above chloro-derivative had been prepared contained some of its 2-nitro-isomeride—these two are very difficult to separate—and consequently the resulting chloro-compound was a corresponding mixture. The supposed 4-chloro-6-nitro-3-hydroxybenzaldehyde is now shown to be the 2-nitro-isomeride (by conversion to 2 : 4-dichloro-3-hydroxybenzaldehyde), and the supposed 4-chloro-2-nitro-3-hydroxybenzaldehyde is really the 2-chloro-4-nitro-compound (identified by mixed m. p. and comparison of semicarbazones and *p*-nitrophenylhydrazones).

EXPERIMENTAL.

Nitration of 6-Nitro-3-hydroxybenzaldehyde.—To the aldehyde (10 g.; m. p. 166°) in glacial acetic acid (30 c.c.) solution at 70°, nitric acid (10 c.c.; *d* 1·42) was added during ¼ hour; the mixture was kept for a further ¼ hour and poured into ice water (150 c.c.); and the voluminous mass of crystals (9 g.; m. p. 71—74°) which slowly separated was extracted with boiling water, which removed 2 : 6-dinitro- from the much less soluble 4 : 6-dinitro-3-hydroxybenzaldehyde.

Nitration of 2-Nitro-3-hydroxybenzaldehyde.—2 G. on similar treatment gave only the above water-soluble product (1·8 g.), identified by a mixed m. p. determination and through the *p*-nitro- and *p*-bromo-phenylhydrazones.

Nitration of 4-Nitro-3-hydroxybenzaldehyde.—The above treatment gave unchanged material only; nitration of a sulphuric acid solution by potassium nitrate (1 mol.) gave a mixture of 4 : 6-dinitro- and 2 : 4 : 6-trinitro-3-hydroxybenzaldehydes with unchanged material, whereas excess of potassium nitrate (2 mols.) gave mainly the trinitro-product. If the finely-powdered aldehyde (10 g.) was added gradually to well-stirred synthetic nitric acid (50 g.; 98%) at 5—10°, and the mixture was allowed to attain room temperature before being poured on ice (250 g.), the trinitro-product (3 g.) separated, and the 4 : 6-dinitro-compound (5·4 g.) could be salted out of solution. Identity of the latter with the less soluble product above was established as in the case of the more soluble product.

2 : 6-*Dinitro-3-hydroxybenzaldehyde* is more soluble in the usual solvents than its 4 : 6-isomeride, and crystallises from water in colourless needles, m. p. 94° (Found: N, 13·3. $C_7H_4O_6N_2$ requires N, 13·2%). On exposure to air, it acquires a deep brown colour, whereas its alcoholic solution turns green. The yellow *sodium* and dark orange *ammonium* salts are both very soluble in water, but the silver salt could not be obtained. The p-*nitrophenylhydrazone*, deep

terra-cotta needles which explode at 240—242°, and the p-*bromophenylhydrazone*, similar crystals, m. p. 166—167° (decomp.) (Found: Br, 20·8. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), were both crystallised from glacial acetic acid.

4 : 6-*Dinitro*-3-*hydroxybenzaldehyde* crystallises from dilute acetic acid in almost colourless needles, m. p. 106° (Found: N, 12·9%). The orange *sodium* and dark orange *ammonium* salts are very soluble in water, but the silver salt could not be prepared. The p-*nitrophenylhydrazone* forms deep reddish-orange needles, which decompose slowly at 282—283°; the p-*bromophenylhydrazone* forms dark crimson needles, m. p. 249—250° (decomp.) (Found: Br, 20·8%).

2 : 4 : 6-*Trinitro*-3-*hydroxybenzaldehyde* is produced when 6-nitro-3-hydroxybenzaldehyde (10 g.) in concentrated sulphuric acid (50 g.) is treated gradually with a mixture of nitric acid (25 c.c.; *d* 1·42) and sulphuric acid (25 c.c.; *d* 1·84) at 70—75°; the cooled mixture is poured on ice (200 g.); the precipitate crystallises from benzene in stout, colourless, hexagonal prisms, m. p. 161—162° (decomp.) (Found: N, 16·7. $C_7H_3O_8N_3$ requires N, 16·3%). The product is much more soluble in water than picric acid. The solutions in alkalis are deep red, although the *sodium* salt crystallises in bright yellow needles. The p-*nitrophenylhydrazone*, dark crimson needles, exploded violently at 228—230°, and the p-*bromophenylhydrazone*, deep olive-green parallelepipeds with metallic lustre, also exploded violently at 218—220° (Found: Br, 18·8. $C_{13}H_8O_7N_5Br$ requires Br, 18·8%). The *azine* was prepared by adding a mixture of hydrazine sulphate (1 g.), sodium hydroxide (3 c.c.; 20%), and water (5 c.c.) to a hot solution of the aldehyde (2 g.) in water (60 c.c.), and separated, on cooling, in bright yellow micro-needles; it is readily soluble in acetic acid (50%) and alcohol, insoluble in benzene and chloroform, and gives red solutions with alkalis; it explodes violently at 150—160°.

2 : 4 : 6-Trinitro-3-hydroxybenzaldehyde was also obtained from 2- and 4-nitro-3-hydroxybenzaldehyde, but the product from the latter was much less pure than in the other cases.

Dinitration of p-*Hydroxybenzaldehyde*.—Mixtures of nitric and sulphuric acids yielded only picric acid, but when 3-nitro-4-hydroxybenzaldehyde (10 g.) was added with stirring to nitric acid (80 g.; 98%) at 5° and the deep red solution was allowed to warm to 10° and then poured on ice (150 g.), a mixture (10 g.) of 3 : 5-dinitro-4-hydroxybenzaldehyde and picric acid was obtained, the latter being eliminated by one crystallisation from glacial acetic acid.

3 : 5-*Dinitro*-4-*hydroxybenzaldehyde* crystallises in colourless needles, m. p. 102—103° (Found: N, 13·1. $C_7H_4O_6N_2$ requires

N, 13·2%), which are moderately soluble in water; the *sodium* salt is pale orange. The p-*nitrophenylhydrazone*, deep orange microcrystals, slowly decomposes at 283—284°; the p-*bromophenylhydrazone*, brick-red needles, decomposes rapidly at 242—244° (Found: Br, 20·9. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%); the *phenylhydrazone*, deep maroon needles, has m. p. 203° (Found: N, 18·6. $C_{13}H_{10}O_5N_4$ requires N, 18·5%).

Some Hydrazones of 3-*Nitro*-4-*hydroxybenzaldehyde*.—These were all crystallised from glacial acetic acid. Phenylhydrazone: dark red needles, m. p. 175—176° (slow decomp.) (Schöpff, *Ber.*, 1891, **24**, 3776, gives m. p. 175—176°). p-*Nitrophenylhydrazone*: dull orange needles, m. p. 247—249° (decomp.) (Found: N, 18·7. $C_{13}H_{10}O_5N_4$ requires N, 18·5%). p-*Bromophenylhydrazone*: bright red needles, m. p. 192—193° (Found: Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%).

Nitration of m-*Methoxybenzaldehyde*.—(a) *Mononitration*. Friedländer and Schreiber's conditions (*loc. cit.*), together with Rieche's test (*loc. cit.*) for the end-point of mononitration, gave no solid products until the temperature was allowed to rise to 20°; 40 g. of *m*-methoxybenzaldehyde then afforded 31g. of nitrated product and 15 g. of unchanged material. By the use of 85% nitric acid, however, 30 g. of nitrated products were obtained from 25 g. of aldehyde; when this yield was dissolved in hot benzene (20 g.) 2-nitro-3-methoxybenzaldehyde (11 g.) was deposited on cooling, and the mother-liquor contained some 6-nitro-3-methoxybenzaldehyde. No 4-nitro-3-methoxybenzaldehyde was ever isolated. Tröger and Fromm's statement (*J. pr. Chem.*, 1925, **111**, 217) that the 6-nitro-isomeride is absent has been shown to be incorrect, inasmuch as 6-nitro-3-methoxybenzoic acid has been isolated after oxidation of the foregoing mixture.

(b) *Dinitration*. Tiemann and Ludwig's conditions (*loc. cit.*) gave small yields accompanied by much charring; better results were obtained as follows: *m*-Methoxybenzaldehyde (10 g.) was added gradually to a mixture of potassium nitrate (17 g.) in concentrated sulphuric acid (80 g.) at 0—5°, then poured on ice, and the resulting colourless solid (12·4 g.) was extracted twice with boiling water, which dissolved Tiemann's β-compound (3 g.; m. p. 110—130°) and left the α-compound, which was almost pure 2 : 6-dinitro-3-methoxybenzaldehyde, m. p. 156—157° after one crystallisation from benzene. The β-compound (3 g.) was dissolved in hot benzene (16 g.), which deposited only 2 : 6-dinitro-3-methoxybenzaldehyde on cooling; the mother-liquor contained chiefly the 4 : 6-dinitro-isomeride. The total yields from the above nitration were 80% of 2 : 6- and 20% of 4 : 6-dinitro-3-methoxybenzaldehydes.

Nitration of 6-*Nitro*-3-*methoxybenzaldehyde*.—The aldehyde (10 g.) was added to nitric acid (100 c.c.; 98%) at 20°, kept for ½ hour, and then poured into ice water. The colourless solid (11·5 g.) which separated was fractionally crystallised from benzene and proved to be mainly 2 : 6- (m. p. 157°) with a little 4 : 6-dinitro-3-methoxybenzaldehyde.

Nitrations of 4- *and* 2-*Nitro*-3-*methoxybenzaldehydes*.—These aldehydes (10 g. each) gave almost pure 4 : 6- (10 g.; m. p. 127—131°) and 2 : 6-dinitro-3-methoxybenzaldehydes (11·5 g.; m. p. 152—156°) which melted at 131° and 157° respectively after one crystallisation from benzene.

2 : 6-*Dinitro*-3-*methoxybenzaldehyde* crystallises from benzene in stout, hexagonal prisms, m. p. 157° (Found : N, 12·4. $C_8H_6O_6N_2$ requires N, 12·3%); 5 g. require 60 g. of boiling benzene for complete solution. The p-*nitrophenylhydrazone* forms pale orange, elongated, hexagonal plates, which explode at about 260°, and the p-*bromophenylhydrazone* terra-cotta needles, m. p. 196—197° (decomp.) (Found : Br, 20·0. $C_{14}H_{11}O_5N_4Br$ requires Br, 20·2%). On being boiled with 50 c.c. of 1% potassium permanganate solution, the aldehyde (1 g.) was oxidised to 2 : 6-*dinitro*-3-*methoxybenzoic acid*. This forms colourless needles, m. p. 199° (Found : N, 11 9. $C_8H_6O_7N_2$ requires N, 11·6%), which give a yellow solution in aqueous sodium carbonate with liberation of carbon dioxide.

4 : 6-*Dinitro*-3-*methoxybenzaldehyde* crystallises from benzene in hexagonal prisms, m. p. 131° (Found : N, 12·3. $C_8H_6O_6N_2$ requires N, 12·3%); 5 g. require 12 g. of boiling benzene for complete solution; p-*nitrophenylhydrazone*, terra-cotta needles, m. p. above 300° without explosion (Found : N, 19·5. $C_{14}H_{11}O_7N_5$ requires N, 19·4%); p-*bromophenylhydrazone*, dull red needles, m. p. 254—256° (decomp.) (Found : Br, 20·3. $C_{14}H_{11}O_5N_4Br$ requires Br, 20·2%). Oxidation as above gave 4 : 6-dinitro-3-methoxybenzoic acid, m. p. 188—189° (Giua, *Gazzetta*, 1915, **45**, 352, gives m. p. 186—187°) (Found : N, 11·8. Calc. : N, 11·6%), which liberates carbon dioxide from sodium carbonate, but much less readily than its isomeride above.

Nitration of 2 : 5-*Dichlorobenzaldehyde*.—The method of Gnehm and Banziger (*Ber.*, 1896, **29**, 876) results in 2 : 5-dichloro-6-nitrobenzaldehyde (3 parts) and a second product (1 part) which has now been diagnosed as 2 : 5-*dichloro*-3-*nitrobenzaldehyde* (by conversion into 2 : 3 : 5-trichlorobenzaldehyde); it forms a *phenylhydrazone*, orange needles, m. p. 171°, and a p-*nitrophenylhydrazone*, deep orange needles, m. p. 290—292° (decomp.). On oxidation with alkaline permanganate, 2 : 5-*dichloro*-3-*nitrobenzoic acid* results; this crystallises from glacial acetic acid in colourless needles, m. p.

220° (the 6-nitro-acid has m. p. 143—144°) (Found: Cl, 30·1. $C_7H_3O_4NCl_2$ requires Cl, 30·0%).

2 : 3 : 5-*Trichlorobenzaldehyde* is volatile in steam, has a characteristic pungent odour, is soluble in the usual organic solvents, and crystallises from dilute alcohol in colourless needles, m. p. 56° (the 2 : 4 : 5-isomeride melts at 110—111°) (Found: Cl, 50·0. $C_7H_3OCl_3$ requires Cl, 50·1%). On oxidation with neutral permanganate, 2 : 3 : 5-trichlorobenzoic acid results, m. p. 162° (Cohen and Dakin, J., 1902, **81**, 1331, give m. p. 162°).

Additional Nitrophenylhydrazones used for Comparison Purposes.—All were crystallised from glacial acetic acid. They are tabulated under the heading of the components from which they were prepared.

Benzaldehyde.	Nitrophenylhydrazine.		M. p.
3-Hydroxy-	*o*	Terra-cotta needles	195°
,,	*m*	Deep crimson needles	209—210
,,	*p*	Terra-cotta needles	219—220
6-Nitro-3-hydroxy-	*o*	Deep terra-cotta needles	248—250 (slow decomp.)
,, ,,	*m*	Scarlet needles	257—258 (slow decomp.)
6-Nitro-3-methoxy-	*p*	Terra-cotta needles	281—283
4- ,, ,,	*p*	Saffron needles	257—258
2- ,, ,,	*p*	Curly orange needles	222—223
2 : 5-Dichloro-6-nitro-	*p*	Fine pale yellow needles	269—270 (decomp.)

Additional p-*Bromophenylhydrazones.*—All were crystallised from glacial acetic acid.

Benzaldehyde.		M. p.
6-Nitro-3-hydroxy-	Reddish-brown, hexagonal clusters	214—215°
4- ,, ,,	Crimson needles	179—180
2- ,, ,,	Nigre-brown needles	194—195 (rapid decomp.)
6-Nitro-3-methoxy-	Light crimson needles	235—236
4- ,, ,,	Pale orange needles	177—178
2- ,, ,,	Orange needles	193—194

Persistence of Colour Effects on Dilution.—Test. 0·01 G. of the hydrazone was treated with 15 c.c. of alcoholic potassium hydroxide (10 g. in 75 g. of solution), and the coloured mixture then gradually diluted with water.

(a) *Nitro-group in phenylhydrazine portion only.* The intense magenta-violet colour of benzaldehyde-*p*-nitrophenylhydrazone was not dispersed until 18,000 c.c. of water had been added.

(b) *Nitro-group in aldehyde portion only.* The deep greenish-blue colour of *p*-nitrobenzaldehydephenylhydrazone required only 35 c.c. of water for its dispersion.

Colours produced by Aqueous and Alcoholic Alkalis.—Test. 0·05 G. of hydrazone was treated with 5 c.c. of 10% aqueous or alcoholic potassium hydroxide. The hydrazones are tabulated as in the previous tables.

Key to abbreviations. S. = same; D. = deeper; N. = no coloration.

Benzaldehyde.	Phenylhydrazine.	Aqueous alkali. Cold.	Aqueous alkali. Hot.	Alcoholic alkali. Cold.	Alcoholic alkali. Hot.
3-Hydroxy-	*o*-Nitro-	Bordeaux.	S.	D. Bordeaux.	D.
„	*m*- „	Yellow.	S.	Yellow.	S.
„	*p*- „	Bordeaux.	S.	D. Bordeaux.	S.
6-Nitro-3-hydroxy-	*o*- „	Orange.	D.	Olive-green.	D.
„ „	*m*- „	N.	Red.	Pale olive-green	D.
„ „	*p*- „	Bordeaux.	S.	Bluish-magenta.	S.
4- „	*p*- „	Bordeaux.	S.	Reddish-violet.	S.
2- „	*p*- „	Bordeaux.	S.	Bluish-magenta.	S.
6-Nitro-3-methoxy-	*p*- „	N.	N.	Blue (trace of red).	D.
4- „ „	*p*- „	N.	N.	Pure cobalt-blue.	S.
2- „ „	*p*- „	N.	N.	Blue (trace of red).	S.
4 : 6-Dinitro-3-hydroxy-	*p*- „	Bordeaux.	S.	Reddish-violet.	S.
2 : 6- „	*p*- „	Bordeaux.	S.	Violet.	D.
4 : 6-Dinitro-3-methoxy-	*p*- „	N.	N.	Bluish-green.	Violet.
2 : 6- „	*p*- „	N.	N.	Cobalt-blue.	S.
2 : 4 : 6-Trinitro-3-hydroxy-	*p*- „	Instantaneous blue quickly fades, giving canary-yellow, very explosive solid (Na salt) and magenta solution.	Blue develops.	Bluish-green.	Bluish-black.
3-Nitro-4-hydroxy-	*p*- „	Magenta.	S.	Magenta.	S.
3 : 5-Dinitro-4-hydroxy-	*p*- „	Magenta.	S.	Magenta.	S.
2 : 5-Dichloro-6-nitro-	*p*- „	N.	N.	Blue.	D.
2 : 5-Dichloro-3-nitro-	*p*- „	N.	N.	Blue.	D.
6-Nitro-3-hydroxy-	*p*-Bromo-	Substance turns from reddish-brown to deep orange, but no solution effect.	S.	Yellow.	S. Green with stronger alkali.
4- „ „	*p*- „	N.	N.	Brown.	Greenish-brown with excess.
2- „ „	*p*- „	Substance turns crimson; solution colourless.	S.	Red solution.	Greenish-brown with excess.
6-Nitro-3-methoxy-	*p*-	N.	N.	Pale green.	D.
4- „ „	*p*- „	N.	N.	Deep green, becoming yellow.	Bluish-green.
2- „ „	*p*- „	N.	N.	N.	Red.
4 : 6-Dinitro-3-hydroxy-	*p*- „	Red.	S.	Olive-green.	D.
2 : 6- „ „	*p*- „	Pale olive-green solution. Deep orange substance.	S.	Deep green.	S.
4 : 6-Dinitro-3-methoxy-	*p*- „	N.	N.	Deep blue.	S.
2 : 6- „	*p*- „	N.	N.	Deep green.	D.
2 : 4 : 6-Trinitro-3-hydroxy-	*p*- „	Substance changes to brownish-red; colourless solution.	S.	Instantaneous bright blue.	Blue-black.
2 : 5-Dichloro-6-nitro-	Unsubstituted.	N. (cf. Chattaway).	N.	Yellow.	Reddish-brown changes to deep red and then to yellow. Colourless solid on dilution with water.
2 : 5-Dichloro-3-nitro-	„	N.	N.	Dark brown.	D.
3-Nitro-4-hydroxy-	*p*-Bromo-	N.	S.	Red.	S.
3 : 5-Dinitro-4-hydroxy-	*p*- „	Substance turns brick red.	S.	Substance turns darker red.	S.
„ „	Unsubstituted.	N.	N.	Red.	S.

(c) *Nitro-groups in both portions.* The intense cobalt-blue colour of *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone became violet with about 25 c.c. of water, magenta with 25—50 c.c., and vanished at 275 c.c.

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 6th*, 1927.]

NOTES.

The Structure of Quinizarin. By ALBERT GREEN.

Two alternative schemes were advanced (J., 1926, 1430) for the reaction between quinizarin and thionyl chloride, the second of which suggested the replacement of a carbonyl oxygen atom by two atoms of chlorine. This is now shown to be improbable, for diacetylquinizarin (4 g.), m. p. 207—208°, after boiling with an excess of thionyl chloride for 2 hours, crystallised in the polymorphic form (3·8 g.), which was free from chlorine and melted, either alone or mixed with an authentic specimen, at 200°.

Although this lack of reactivity on the part of a derivative, in which the probably mobile hydrogens of the hydroxyl groups are replaced, would appear to invalidate the second mechanism suggested for the formation of 10-chloro-1-hydroxy-4 : 9-anthraquinone from quinizarin, it should not be held to dispose of it entirely, since there are many examples of carbonyl groups in free hydroxyanthraquinones showing properties different from those they display in simple derivatives. The *meso*-carbonyl groups influence, and are influenced by, substituents in the α-positions of anthraquinones : *e.g.*, whilst anthraquinone itself yields an oxime only with difficulty, 1-chloroanthraquinone easily gives the oxime; 1-hydroxyanthraquinone cannot be oximated, yet its ethers yield monoximes (Freund and Achenbach, *Ber.*, 1910, **43**, 3251).

Whilst it is clear, therefore, that any deduction from an experimental result obtained with an alkylated or acylated hydroxyanthraquinone should be applied to the hydroxy-compound itself with caution, nevertheless the work described above strengthens the first suggestion (*loc. cit.*), that quinizarin assumes a reactive *ortho*-quinonoid state (1 : 10-dihydroxy-4 : 9-anthraquinone) when it reacts with thionyl chloride to yield 10-chloro-1-hydroxy-4 : 9-anthraquinone. Furthermore, in this reaction only one of the hydroxyl groups is affected, and this affords experimental support

for the suggestion of Perkin (J., 1899, **75**, 433) that, although the two hydroxyls of quinizarin, under suitable conditions, may assume a double quinonoid change, in the case of the second hydroxyl group this change is not readily achieved and is of an unstable nature.

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Solubility of Cupric Sulphide in Alkali Sulphides in Presence of Sulpharsenates. By CHRISTINA DAVIES and ALEXANDER DONALD MONRO.

ALTHOUGH the slight solubility of cupric sulphide in yellow ammonium sulphide is well known, the enhanced solubility in presence of metals of the arsenic group has been little studied. Wohler (*Annalen*, 1840, **34**, 236) and Storch (*Ber.*, 1883, **16**, 2015) have shown that the sulpho-salts of these acids promote the solubility of cupric sulphide, but as no quantitative data were available a further study of the Cu–As system was made.

Solutions of various quantities of arsenic trioxide in hydrochloric acid were diluted and to each was added a solution containing 0·200 g. of copper. The mixture was completely precipitated as sulphide, which was filtered off, washed, and warmed with 50 c.c. of yellow ammonium sulphide [78·47 g. of sulphur and 73·26 g. of ammonia per litre, *i.e.*, approximately $(NH_4)_2S_2$]. The resulting mixture was filtered, and the filtrate treated with hydrochloric acid to precipitate copper and arsenic sulphides. After another filtration the precipitate was treated with warm dilute nitric acid to separate the copper, which, after evaporation with sulphuric acid, was precipitated and weighed as thiocyanate. The following results were obtained :

As present (mg.) ...	0	83·3	113·6	253·2	254·5	265·2	349·7	613·5
Cu dissolved (mg.)..	7·8	29·5	34·5	52·0	52·2	53·0	61·0	80·4

The amount of copper dissolved rises steadily with increasing amounts of arsenic until it becomes ten times its original value. This agrees with our observation that it is possible for small amounts of copper in copper–arsenic mixtures to be entirely missed in a qualitative analysis, unless the arsenic group is examined for copper.

A second series was tried in which colourless ammonium sulphide was substituted for yellow ammonium sulphide. No copper was found in the arsenic filtrate. Pure sodium sulphide gave irregular results. With 0·1600 g. of arsenic, 0·0373 g. of copper appeared

in the filtrates, but although two other results gave appreciable dissolved copper, other experiments gave negative results. Qualitative experiments showed that copper sulphide dissolved appreciably in presence of arsenic sulphide, giving unstable solutions from which cupric sulphide was reprecipitated on warming.

A solution of sodium polysulphide (16 g. of sulphur and 120 g. of $Na_2S,9H_2O$ per litre, *i.e.*, Na_2S_2) gave stable solutions containing arsenic and copper. The influence of arsenic was not so great as in the first series of experiments, but was by no means negligible. The results were as follows:

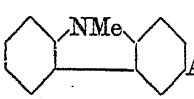
Cu taken, 0·200 g.; 50 c.c. of Na_2S_2 solution.

As (mg.)	0	149·2	237·7	365·5	480·0	620·2
Cu diss. (mg.).....	41·8	48·5	50·7	51·8	52·0	53·0

—UNIVERSITY OF GLASGOW. [*Received, June 25th*, 1927.]

9-*Methylcarbazole*-3-*arsinic Acid and its Reduction Products.* By HAROLD BURTON and CHARLES STANLEY GIBSON.

3-AMINO-9-METHYLCARBAZOLE was prepared from 9-methylcarbazole (Burton and Gibson, J., 1924, **125**, 2501) by nitration in acetic acid solution and reduction of the 3-nitro-9-methylcarbazole by means of tin and hydrochloric acid (Lindemann, *Ber.*, 1924, **57**, 555; Morgan and Read, J., 1922, **121**, 2715). It was characterised by its m. p., 173—174°, and by its acetyl derivative, m. p. 208—209° (Found: C, 75·65; H, 5·65. Calc.: C, 75·6; H, 5·9%). Lindemann (*loc. cit.*) gives m. p.'s 174° and 210°, respectively. On diazotisation in hydrochloric acid solution at the ordinary temperature (compare Morgan and Read, *loc. cit.*) and addition of an alkaline solution of β-naphthol, the deep red 9-*methylcarbazole*-3-*azo*-β-*naphthol* separated. This compound was obtained from its solution in acetic acid in small, deep red needles, m. p. 212° (decomp.) (Found: C, 78·5; H, 5·2; N, 12·1. $C_{23}H_{17}ON_3$ requires C, 78·6; H, 4·9; N, 12·0%).

9-*Methylcarbazole*-3-*arsinic Acid*,  .—A suspension of 3-amino-9-methylcarbazole (19·6 g.) in a mixture of water (250 c.c.) and concentrated hydrochloric acid (25 c.c.) was cooled below 10° and diazotised with sodium nitrite solution. The diazo-solution was then cooled to 0° and neutralised with cold sodium hydroxide solution. The neutralised solution was added gradually with stirring at room temperature to a solution of sodium arsenite (arsenious oxide, 15 g.; sodium carbonate, 24 g.; water, 105 c.c.), to which 10 c.c. of a 10% solution of copper sulphate

previously treated with ammonia had been added. After the addition was complete, the mixture was stirred for 1 hour, boiled, and filtered from tarry matter. The filtrate on acidification deposited the crude acid (10·5 g.); this crystallised from glacial acetic acid in clusters of small, colourless needles, which did not melt below 300° (Found: As, 24·3. $C_{13}H_{12}O_3NAs$ requires As, 24·6%).

9-*Methylcarbazole*-3-*arsenious Chloride*.—A boiling solution of 9-methylcarbazole-3-arsinic acid (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine was saturated with sulphur dioxide for 10 minutes. On cooling, the crude *chloroarsine* separated as a gummy mass which gradually solidified. It was purified by dissolving it in benzene, adding light petroleum to the hot solution until all the colouring matter was precipitated, and then filtering and cooling it; the chloroarsine separated in small, colourless prisms, m. p. 121—122° (Found: As, 22·6. $C_{13}H_{10}NCl_2As$ requires As, 23·0%).

9-*Methylcarbazole*-3-*arsenious Oxide*.—A solution of the chloroarsine in acetone was treated with ammonia, and the mixture well shaken. The precipitate was filtered off, washed with water until free from chloride, and dried. The *oxide* is insoluble in the ordinary organic solvents. It has m. p. 182—185° (decomp.) (Found: As, 27·3. $C_{13}H_{10}ONAs$ requires As, 27·7%).—Guy's Hospital Medical School (University of London), S.E.1. [*Received, July 26th*, 1927.]

Derivatives of o-*Aminophenylarsinic Acid*. By Harold Burton and Charles Stanley Gibson.

During the course of investigations which have been carried out on heterocyclic arsenic compounds, a number of simple arsinic compounds have been prepared which might be useful to other investigators.

o-*Ethylaminophenylarsinic Acid*, $NHEt{\cdot}C_6H_4{\cdot}AsO(OH)_2$.—Ethyl sulphate (17 g.) was added to a constantly stirred solution of *o*-aminophenylarsinic acid (21·7 g.) in sodium hydroxide solution (45 c.c., 10%), heated on the water-bath, and the clear solution heated for 10 minutes after the initial reaction had finished. The red oil which separated on cooling solidified and was recrystallised from water, forming colourless needles, m. p. 128—129° (yield, 6 g.) (Found: As, 30·7. $C_8H_{12}O_3NAs$ requires As, 30·6%). The *nitroso*-derivative was prepared by adding a solution of sodium nitrite (2·5 g.) to a solution of the acid (2 g.) in dilute hydrochloric acid. The crystalline product (1·7 g.), which gave Liebermann's nitrosoamine-reaction, was recrystallised from water and obtained in colourless needles, m. p. 160° (decomp.) (Found: As, 27·0.

$C_8H_{11}O_4N_2As$ requires As, 27·35%). The *acetyl* derivative (m. p. 187—188°), prepared in the usual way, was readily soluble in water and in the common organic solvents; its *silver* salt was analysed and the acid shown to be dibasic (Found: Ag, 43·0. $C_{10}H_{12}O_4NAsAg_2$ requires Ag, 43·1%).

3-*Nitro*-6-*diethylaminophenylarsinic Acid*,

$$NEt_2 \cdot C_6H_3(NO_2) \cdot AsO(OH)_2.$$

—For the preparation of this acid we required 4-*nitro*-2-*aminodiethylaniline*. This was prepared by the ammonium sulphide reduction of 2 : 4-dinitrodiethylaniline, and the product isolated as the crystalline *hydrochloride*, yellow prisms, m. p. 205—206°. The *benzylidene* derivative formed yellow needles, m. p. 97—98°, from alcohol (Found: C, 68·4; H, 6·6. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·4%). The base itself was obtained as a red, viscous oil. The hydrochloride was suspended in water, diazotised, and reduced with sodium stannite, giving *p*-nitrodiethylaniline, m. p. 75°.

A mixture of 4-nitro-2-aminodiethylaniline hydrochloride (24·5 g.), water (150 c.c.), and concentrated hydrochloric acid (25 c.c.) was diazotised at 0° with a sodium nitrite solution (7 g.; 20 c.c.). This diazo-solution was added to a stirred solution consisting of sodium arsenite (arsenious oxide, 15 g.; crystalline sodium carbonate, 65 g.; water, 105 c.c.; 5*N*-sodium hydroxide, 40 c.c.) and 10 c.c. of a 10% solution of copper sulphate which had been treated with an excess of ammonia. The mixture was stirred until frothing had subsided and then warmed until all effervescence had ceased. After cooling, it was stirred with decolorising charcoal, filtered, and the filtrate acidified with hydrochloric acid (Congo-red). The acid (5·5 g.) was filtered off and crystallised from a large volume of water, from which it separated in glistening, yellow needles, m. p. 195—196° (decomp.) (Found: As, 23·5. $C_{10}H_{15}O_5N_2As$ requires As, 23·6%).

3-*Nitro*-6-*diethylaminophenylarsenious Chloride*,

$$NEt_2 \cdot C_6H_3(NO_2) \cdot AsCl_2.$$

—3-Nitro-6-diethylaminophenylarsinic acid (3·2 g.), in alcohol (20 c.c.) and concentrated hydrochloric acid (10 c.c.) containing a trace of iodine, was saturated with sulphur dioxide for 30 minutes. On cooling, a yellow, crystalline product separated (3·0 g.); this crystallised from benzene in deep yellow prisms, m. p. 143—144° (Found: As, 22·1; Cl, 20·8. $C_{10}H_{13}O_2N_2Cl_2As$ requires As, 22·1; Cl, 20·9%).

When *o*-ethylaminophenylarsinic acid or its acetyl derivative was reduced under similar conditions, arsenic was eliminated from the molecule.—GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), S.E.1. [*Received, July 26th*, 1927.]

CCCXX.—*Strychnine and Brucine. Part VI. The Catalytic Hydrogenation of Strychnine and Some Derivatives.*

By ALBERT EDWARD OXFORD, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

THE motive of this investigation was our desire to gain further knowledge of the function of the characteristic groups and of the nitrogen and oxygen atoms in the molecule of strychnine, and we directed our attention in the first place to the question of the unsaturated centres. The results show clearly that strychnine contains one double bond. According to Skita and Franck (*Ber.*, 1911, **44**, 2863), the reduction of strychnine in dilute acetic acid solution by means of hydrogen in presence of palladium (from 1% palladous chloride in presence of gum arabic) yields a dihydrostrychnine, m. p. 209—210°, but the volume of hydrogen stated to have been absorbed is only about half of that theoretically required. Owing to an erroneous calculation of the latter, Skita and Franck considered that the correct amount had been absorbed. Repetition of the experiment under the conditions employed by these authors gave negative results, but under other conditions we obtained *dihydrostrychnine*, $C_{21}H_{24}O_2N_2$, which crystallised well from aqueous methyl alcohol with $2H_2O$, and when anhydrous had m. p. 220—222°. Skita and Franck make no mention of the water of crystallisation, and they state, further, that the catalytic reduction of strychnine under 3 atm. pressure at 70° yields tetrahydrostrychnine, identical with the substance obtained by the electrolytic reduction of strychnine. It is certain, at least, that our dihydrostrychnine could not be an intermediate product in the latter process. Just as strychnine, $C_{21}H_{22}O_2N_2$, by electrolytic reduction yields strychnidine, $C_{21}H_{24}ON_2$, and tetrahydrostrychnine, $C_{21}H_{26}O_2N_2$, by conversion of ·CO·N: into ·CH_2·N: and ·CH_2(OH) + NH:, respectively (Tafel, *Annalen*, 1898, **301**, 301), so, in the same manner, dihydrostrychnine yields *dihydrostrychnidine* (A),* $C_{21}H_{26}ON_2$, m. p. 212—214°, and *hexahydrostrychnine*, $C_{21}H_{28}O_2N_2$, m. p. 197—199°. Furthermore, catalytic reduction of strychnidine gave dihydrostrychnidine (A) and catalytic reduction of tetra-

* Two dihydrostrychnidines, $C_{21}H_{26}ON_2$, have been prepared during the course of our investigations, and we propose to designate by (A) the substance described in the present communication, m. p. 212—214°. The isomeric dihydrostrychnidine (B) melts at 151° and is obtained from strychnidine by reduction with hydriodic acid and phosphorus. An account of the interesting properties of this substance will form the subject of a communication to be published in the near future.

hydrostrychnine gave hexahydrostrychnine, identical with the bases already mentioned. The dehydration of tetrahydrostrychnine to strychnidine is also paralleled by the similar conversion of hexahydrostrychnine into dihydrostrychnidine (A). The further reduction of these substances by hydrogen in presence of catalysts could not be accomplished, and dihydrostrychnine is characterised by its stability towards oxidising agents. It seems certain that the strychnine molecule contains only one double bond, and Tafel's view of the relation of strychnine to strychnidine and tetrahydrostrychnine is amply confirmed. Although, therefore, dihydrostrychnine contains the ·CO·N: group, we have not found it possible to demonstrate this by the preparation of dihydrostrychnic acid, and it is evident that the reduction has stabilised the lactam ring. At one point, we have made a contact with the investigation described in Part IV (this vol., p. 1617), since *dihydrostrychnidine* (A) *methosulphate* yields methoxymethyltetrahydrostrychnidine, m. p. 220°, when it is heated with methyl-alcoholic potassium hydroxide. Methoxymethyltetrahydrostrychnidine was previously obtained by electrolytic reduction of methoxymethyldihydrostrychnidine, m. p. 126° (*loc. cit.*), the product of the action of methyl-alcoholic potash on strychnidine methosulphate. It is evident that the double bond which resists electrolytic reduction in strychnidine may be readily saturated when methoxymethyldihydrostrychnidine is submitted to the same treatment.

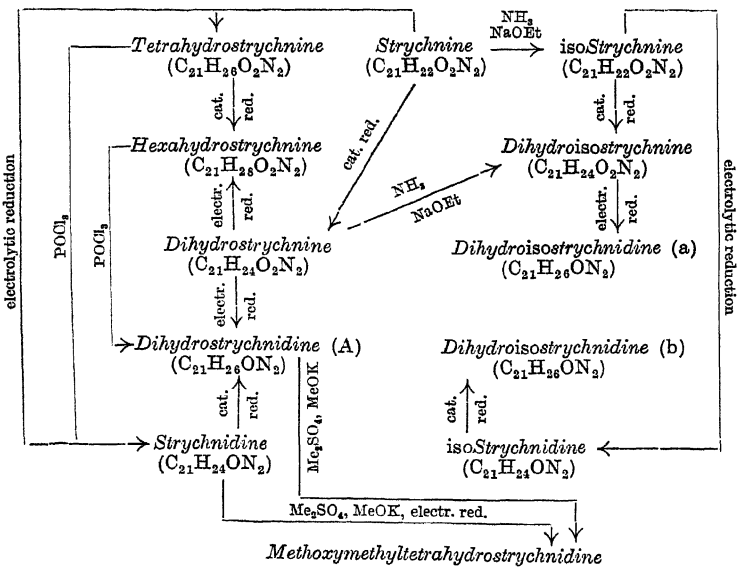
The examination of dihydrostrychnine has led us to consider further the important problem of the relation of strychnine to *iso*strychnine. On catalytic reduction *iso*strychnine yields *dihydro*iso*strychnine*, $C_{21}H_{24}O_2N_2,3H_2O$, m. p. 249—251°, and the same substance was more readily obtained from dihydrostrychnine by the action of warm alcoholic sodium ethoxide. This proves that the strychnine–*iso*strychnine isomerism in no way depends on a shift of the double bond, as had previously been assumed, and that the process involved in the conversion of strychnine into *iso*strychnine does not even require the presence of the double bond. All attempts to prepare acetyl and other similar derivatives of strychnine, strychnidine, dihydrostrychnine, and dihydrostrychnidine (A) have failed, but both *iso*strychnine and dihydro*iso*strychnine yield monoacetyl derivatives. There is no evidence of the presence of imino-groups, and since the *acetyliso**strychnine* and *acetyldihydroiso**strychnine* are strong bases, they must be *O*-acetyl derivatives. Hence the interesting fact emerges that the change of strychnine to *iso*strychnine and of dihydrostrychnine into dihydro*iso*strychnine involves the appearance of a hydroxyl group. On the assumption, therefore, that *iso*strychnine contains

the group ·CO·N: (see below), we know that the other groups in the molecule include a tertiary basic nitrogen atom, one double bond, and a hydroxyl group. It is of fundamental importance that *iso*strychnine contains only one double bond because oxygen can only occur as C:O, C·O·C, or C·OH, and if a substance containing a carbonyl or an ether group isomerises with the production of an alcohol the process must be accompanied by the formation of a new double bond or a new ring. Experiment excludes the former alternative and we must therefore accept the latter. On the hypothesis that strychnine contains an ether group, it becomes necessary to assume the occurrence of some such process as the slipping of a bond in pentamethylene oxide with formation of a hydroxy*cyclo*pentane. This does not commend itself as a probable explanation: there are few analogous reactions and we cannot imagine that such a change would be brought about by the agency of sodium ethoxide in warm alcoholic solution. On the hypothesis that strychnine contains a carbonyl group, however, we can readily explain the appearance of a hydroxyl group in *iso*strychnine as due to an intramolecular condensation, :CO + CH: ⟶ :C(OH)·C:. It is interesting that no parallel to the strychnine–*iso*strychnine transformation exists in the strychnidine and tetrahydrostrychnine series (see p. 2407), and this suggests that the ·CO·N: group is directly concerned. If it should be proved in the future that strychnine is a ketone, then an acceptable explanation of the change of strychnine to *iso*strychnine is that expressed in the scheme

$$:CO + \dot{C}H\cdot CO\cdot N: \longrightarrow :C(OH)\cdot\dot{C}\cdot CO\cdot N:$$

These considerations have necessitated the further examination of the reactions of *iso*strychnine. As stated above, it yields an *O*-acetyl derivative, but we have been unable to confirm the statement of Oliveri-Mandalà and Comella (*Gazzetta*, 1923, **53**, 627) that the base gives a crystalline semicarbazone, m. p. 215° (decomp.). In addition we were unable to obtain a phenylhydrazone of *iso*strychnine or a semicarbazone of dihydro*iso*strychnine. The argument presented above, and indeed any theory implying that the hydroxyl group of *iso*strychnine is derived by modification of the function of the cryptic oxygen atom of strychnine (*i.e.*, that oxygen atom not included in the ·CO·N: group), can only be sustained if *iso*strychnine contains the ·CO·N: group of strychnine. In favour of this view we may marshal the facts that *iso*strychnine is a monoacid base, that it exhibits colour reactions of the strychnine type, that it yields *iso*strychnic acid on hydrolysis (Pictet and Bacovescu, *Ber.*, 1905, **38**, 2787; compare p. 2395), although the reverse change has not been accomplished, and that *iso*strychnic acid

exhibits colour reactions of the strychnidine type; nothing is known that is not in agreement with the suggestion that *iso*strychnine contains this group. We have sought further confirmation by studying the electrolytic reduction of *iso*strychnine and of dihydro*iso*strychnine, and have obtained new bases of the strychnidine type, *viz.*, iso*strychnidine*, $C_{21}H_{24}ON_2,1{\cdot}5H_2O$, and *dihydro*iso*strychnidine*, $C_{21}H_{26}ON_2,0{\cdot}5H_2O$, respectively. The latter must be designated *dihydro*iso*strychnidine* (*a*), since an isomeride, *dihydro*iso*strychnidine* (*b*), is obtained by the catalytic reduction of *iso*strychnidine. These bases exhibit many of the characteristics of strychnidine, and their preparation affords strong support to the view that *iso*strychnine contains the cyclic amide grouping.



The following miscellaneous observations are included in this communication. Some further work on the coupling of strychnine derivatives with diazonium salts has been carried out. Reduction of *sulphobenzeneazostrychnidine* gives *aminostrychnidine*, $C_{21}H_{25}ON_3$, and the striking colour reactions of this base establish beyond question that it is p-*aminostrychnidine*, the amino-group being in the para-relation to the nitrogen atom attached to the benzene nucleus in strychnine. It is, for example, convertible into an analogue of toluylene-blue and then into the eurhodine analogous to toluylene-red.

The Schotten–Baumann benzoylation of strychnic acid was

expected to attack the :NH group that this substance is supposed to contain, and although we have isolated a definite product of the correct composition, yet its behaviour suggests that it is the mixed *anhydride* of benzoic and strychnic acids rather than *N*-benzoylstrychnic acid.

In the course of abortive attempts to convert strychnidine and tetrahydrostrychnine into members of the *iso*strychnine series, it was found that on being heated with water in an autoclave at 170—185° each of these bases was partly converted into an oxidation product.

The scheme on page 2392 summarises the relationships of some of the substances discussed above. A more detailed examination of certain of the new bases now described is in progress, and the work is being extended to the brucine series.

EXPERIMENTAL.

Dihydrostrychnine.—All the catalytic reductions described in this communication were carried out in a flask fitted with an efficient stirrer with gas-tight packing. Norite (50 g., previously heated to redness) was added to a solution of palladous chloride (4 g.) in water (400 c.c.) containing a few drops of concentrated hydrochloric acid, and the mixture stirred in hydrogen until no further absorption took place. A solution of strychnine (57 g.) in 50% acetic acid (200 c.c.) was then introduced and agitation continued for 3—4 hours, during which 3,600 c.c. of hydrogen were absorbed (calc. for one double bond: 3,820 c.c.). The filtered liquid was basified with ammonia, whereupon practically pure *dihydrostrychnine* was precipitated in a crystalline condition (yield, 93%). The recovered catalyst may be reactivated by exposure to the air for a day and can be used at least 4 times, but in any one experiment 1 g. of palladous chloride is unable to catalyse satisfactorily the reduction of more than 17 g. of strychnine.

Dihydrostrychnine crystallises from 50% aqueous methyl alcohol in long, silky, colourless needles (Found: C, 68·3, 67·9; H, 7·5, 7·4; N, 7·1; loss at 100°, 9·3; loss at 130°, 9·8. $C_{21}H_{24}O_2N_2,2H_2O$ requires C, 67·7; H, 7·5; N, 7·5; $2H_2O$, 9·7%). The anhydrous base melts without decomposition at 220—222° (Found: C, 75·1; H, 7·1. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·2%). It dissolves in about 190 parts of boiling water and is sparingly soluble in cold water; it is readily soluble in cold ethyl and methyl alcohols, moderately readily soluble in cold benzene, and sparingly soluble in cold ethyl acetate and in boiling acetone, from which it separates in minute, compact prisms. The substance has a bitter taste similar to that of strychnine. The faintly acid solutions of dihydro-

strychnine develop no coloration on the addition of ferric chloride, and the base does not couple with diazobenzenesulphonic acid. With 60% sulphuric acid (by vol.) and potassium dichromate it gives an intense reddish-purple colour, slowly fading to a brownish-red. Attempts to obtain a semicarbazone of the base were fruitless, and failure also attended an attempt to acetylate it by means of anhydrous sodium acetate and acetic anhydride, the dihydrostrychnine being recovered unchanged and identified by analysis (Found : C, 68·0; H, 7·6; N, 7·5%), by m. p., and by mixed m. p. (220° in each case).

If the base contained the ·CH(OH)· group it should yield a ketone under the conditions used to change codeine into codeinone (Ach and Knorr, *Ber.*, 1903, **36**, 3070). Dihydrostrychnine (5 g.) was dissolved in a cold mixture of concentrated sulphuric acid (3·5 c.c.) and water (31 c.c.); addition of finely powdered potassium dichromate (3 g.) with stirring produced an orange-coloured precipitate, and when the mixture was heated for 20 minutes on the steam-bath a deep brownish-red solution was obtained, from which 4 g. of pure dihydrostrychnine could then be recovered.

Oxidation of the base with potassium permanganate was attempted under the conditions prescribed by Leuchs and Schwabel (*Ber.*, 1913, **46**, 3695) for the oxidation of strychnine. Dihydrostrychnine dihydrate (15 g.), dissolved in chloroform (120 c.c.) and acetone (600 c.c.), was stirred with a little finely powdered potassium permanganate for 1 hour. Oxidation did not occur and the mixture was boiled for 3 hours with gradual addition of potassium permanganate (30 g.), and then for 1 hour longer. The permanganate was destroyed, but 12 g. of dihydrostrychnine were recovered, and the working up of the manganese precipitate gave only a minute amount of a brown syrup that was not further investigated.

Further catalytic hydrogenation of dihydrostrychnine was attempted at 100°, 0·6 g. of palladous chloride being used for 3 g. of the base. No absorption of hydrogen occurred, and the whole of the base was recovered unchanged. Attempts to convert dihydrostrychnine into dihydrostrychnic acid (*e.g.*, by the method used by Tafel, *Annalen*, 1891, **264**, 50, for the conversion of strychnine into strychnic acid free from *iso*strychnic acid) gave either dihydro*iso*strychnine (see below) or an amorphous base melting over a wide range, but in no case was any satisfactory acid product isolated. It may be mentioned here that the catalytic reduction of strychnic acid in dilute acetic acid solution gave dihydrostrychnine in good yield, but in all probability the strychnic acid was first converted into strychnine and then reduced.

Dihydrostrychnine Methosulphate.—A mixture of dihydrostrych-

nine (10 g.), methyl sulphate (6 c.c.), and benzene (120 c.c.) was boiled for 5 minutes, then cooled; the resulting solid crystallised from alcohol in fine, colourless rods, m. p. 322° (decomp.) with previous darkening from 300° (Found : C, 59·1 ; H, 6·4. $C_{23}H_{30}O_6N_2S$ requires C, 59·7 ; H, 6·5%). This derivative is readily soluble in water, but very sparingly soluble in cold alcohol or boiling ethyl acetate or acetone. When it was reduced in aqueous solution by 4% sodium amalgam (under conditions similar to those employed for strychnine methosulphate in experiments that will shortly be reported), no oily base separated and the brownish-red solution was not further investigated. The related *methiodide* was obtained in a similar manner by direct combination of the components. It is moderately readily soluble in water, very sparingly soluble in alcohol, and crystallises from a mixture of these solvents in stellar aggregates of colourless rods, that suffer slight discoloration between 300° and 330° (Found : C, 53·8; H, 5·6. $C_{22}H_{27}O_2N_2I,H_2O$ requires C, 53·2; H, 5·8%).

iso*Strychnine and* iso*Strychnic Acid.*—An attempt to repeat the preparation of the semicarbazone described by Oliveri-Mandalà and Comella (*loc. cit.*) did not succeed, and *iso*strychnine was recovered unchanged (Found : C, 65·5; H, 7·2. Calc. for $C_{21}H_{22}O_2N_2,3H_2O$: C, 65·0; H, 7·2%). No other result was obtained when the sodium hydroxide prescribed by the above-mentioned authors was replaced by a large excess of sodium acetate. When the base (1 g.), together with phenylhydrazine (0·4 g.) and 6% acetic acid (3·5 c.c.), was heated for 3 hours on the steam-bath, the recoverable crystalline base was found to be unchanged *iso*strychnine, m. p. 220°, alone or mixed with an authentic specimen.

The colour reaction of *iso*strychnine with 60% sulphuric acid and potassium dichromate differs somewhat from that of strychnine. It is a not very intense pure violet coloration, fading in a few seconds to a very pale brown. The conversion of *iso*strychnine into *iso*strychnic acid can be accomplished according to Pictet and Bacovescu (*loc. cit.*) by the action of boiling alcoholic sodium ethoxide (concentration not stated) during 6 hours. We find, however, that the yield is very small under their conditions. A mixture of *iso*strychnine trihydrate (4·5 g.) and alcoholic sodium ethoxide (from 0·7 g. of sodium and 7·5 c.c. of alcohol) was heated on the steam-bath for 6¼ hours, giving a deep brownish-red solution that exhibited a green fluorescence. After dilution with water (85 c.c.) and keeping for some hours in the ice-chest, nothing separated and the solution was exactly neutralised with acetic acid. The slimy, red precipitate consisted chiefly of an insoluble pigment

and was extracted with hot water (charcoal); ultimately, colourless, slender needles of *iso*strychnic acid (0·5 g.), m. p. 231° (decomp.), were isolated. The yield was increased to 40% when the hydrolysis was carried out for 11 hours at 60°. This material does not lose weight when heated at 140° for several hours (Found: C, 68·3; H, 7·1. Calc. for $C_{21}H_{26}O_4N_2$: C, 68·1; H, 7·0). We have found that *iso*strychnic acid cannot be reduced by hydrogen in presence of palladinised charcoal in dilute acetic acid solution. It is usually regarded as $C_{21}H_{24}O_3N_2,H_2O$, but the facts suggest that the molecule of water may be constitutionally bound, *e.g.*, by addition to the ethylene linkage. The acid is unchanged by boiling dilute hydrochloric acid and under no conditions has it been reconverted into *iso*strychnine. The colour reactions indicate that the N–CO link has been broken, since they are of the strychnidine type. With ferric chloride in dilute hydrochloric acid solution a red colour develops slowly in the cold, but, on warming, the solution becomes intensely blood-red. Coupling with diazobenzenesulphonic acid occurs in cold dilute acetic acid solution to an azo-compound exhibiting the usual properties. Unlike strychnic acid (see below), *iso*strychnic acid could not be converted into a benzoyl derivative by the Schotten–Baumann method.

O-*Acetyl*iso*strychnine*.—Oliveri-Mandalà and Comella (*loc. cit.*) found that *iso*strychnine, but not strychnine, reacts with magnesium ethyl bromide, yielding a molecular proportion of ethane. They attributed this to interaction of the Grignard reagent with an imino-group in the base; it seems more probable to us that the liberation of ethane is due to the presence of a hydroxyl group in the *iso*-strychnine molecule, and we can recall no evidence indicating that the substance is a secondary base.

A mixture of *iso*strychnine (2 g.), fused sodium acetate (1 g.), and acetic anhydride (6 c.c.) was heated on the steam-bath for 4 hours and considerable darkening occurred. The cooled mass was added to water, and the excess of acetic acid neutralised by sodium bicarbonate. The product was isolated by means of chloroform and crystallised repeatedly from light petroleum, a process which greatly diminishes the final yield. The *acetyl* derivative crystallises in groups of minute, colourless needles, m. p. 133—134° (Found: C, 73·3; H. 6·4. $C_{23}H_{24}O_3N_2$ requires C, 73·4; H, 6·4%); it is readily soluble in most organic solvents and dissolves at once in very dilute acetic acid, the addition of sodium hydroxide then producing a turbidity which soon clears, doubtless as the result of hydrolysis.

*Preparation of Dihydro*iso*strychnine*.—(A) *By the catalytic reduction of* iso*strychnine*. Norite (12 g.) was palladinised (0·5 g. of

palladous chloride in 250 c.c. of water) as already described, and a solution of *iso*strychnine trihydrate (4·9 g.) in a few c.c. of dilute acetic acid was then introduced. The theoretical volume of hydrogen (340 c.c.) was absorbed in 5 hours; absorption then ceased suddenly. The filtered liquid was basified with dilute aqueous sodium hydroxide, a colourless oil being precipitated which solidified after being kept for a long time. The *dihydroisostrychnine* was crystallised from benzene–light petroleum and then several times from water; fern-like bunches of coarse, colourless needles, m. p. 244—246°, were thus obtained (Found: C, 64·7; H, 7·5. $C_{21}H_{24}O_2N_2,3H_2O$ requires C, 64·6; H, 7·7; $3H_2O$, 13·8%).

(B) *By isomeric change of dihydrostrychnine.* Strychnine has been converted into *iso*strychnine in two ways: (1) by heating with water at 170—175° (Pictet and Bacovescu, *loc. cit.*; compare also Leuchs and Nitschke, *Ber.*, 1922, **55**, 3171, and Oliveri-Mandalà and Comella, *loc. cit.*); (2) by heating with methyl-alcoholic ammonia under various conditions (Leuchs and Nitschke, *loc. cit.*). A third method (3) is indicated by the observation of Tafel (*Annalen*, 1891, **264**, 50) that strychnine yields *iso*strychnic acid as well as strychnic acid when it is heated with alcoholic sodium ethoxide at temperatures above 70°. The three processes have been applied to the transformation of dihydrostrychnine.

(1) Dihydrostrychnine (1 g.) and water (25 c.c.) were heated in a sealed tube at 165—185° for 5 hours. Very little decomposition occurred (distinction from strychnine), and the aqueous solution was separated from the gummy residue and kept in the ice-chest. The gum solidified and was found to consist of unchanged material, whilst the solution deposited amorphous material which could be crystallised from water in slender, colourless needles, m. p. 237—238°. This product is slightly impure dihydro*iso*strychnine, as was proved by comparison with specimens prepared by other methods.

(2) This method gave quite good results on a small scale, but an attempt to reproduce the conditions on a larger scale in an autoclave failed completely. A sealed tube containing dihydrostrychnine dihydrate (1·2 g.) and 25 c.c. of methyl-alcoholic ammonia (saturated at 15°) was heated at 120—140° (but not higher) for 48 hours. The tube was opened and the pale yellow liquid evaporated in a vacuum; the residue crystallised from water in colourless needles, m. p. 240—245° (Found: C, 64·8; H, 7·8%).

(3) This is the most satisfactory method of preparation, but the yield is greatly diminished if the operation is carried out on a larger scale. Dihydrostrychnine dihydrate (5 g., finely powdered) was added to an alcoholic solution (20 c.c.) of sodium ethoxide (0·5 g. of sodium), and the mixture heated on the steam-bath

until complete solution had been effected. The deep purplish-red liquid was boiled for 2 minutes, then cooled and maintained at 44—46° for 6 hours. A yellow solid soon began to separate and eventually the liquid became filled with the crystals, forming a thick paste. After being cooled and kept in the ice-chest, the solid was collected, washed with a little alcohol, and dried (2 g., or 40%). Nothing further could be obtained from the alcoholic filtrate, which gave an amorphous precipitate on dilution with water. The base crystallised from water in bunches of colourless needles, m. p. 248—250° (Found: C, 65·1; H, 7·5; loss at 120°, 13·5%). The anhydrous base crystallised from benzene–light petroleum in needles, m. p. 249—251° (Found: C, 74·6; H, 7·2. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·2%).

The following mixtures had melting points that were higher than those of the lower-melting specimens in each case, the m. p.'s of the specimens being those already quoted above: (A) with (B2), (A) with (B3), (B2) with (B3).

Dihydro*iso*strychnine dissolves in 90—100 parts of boiling water and is sparingly soluble in cold water, cold ethyl alcohol, boiling benzene or acetone; it is moderately readily soluble in boiling ethyl acetate, and readily soluble in chloroform, cold methyl alcohol, and hot ethyl alcohol. It gives no ferric chloride reaction, and addition of potassium dichromate to its solution in 60% sulphuric acid produces an intense purple coloration, persisting for a minute and then fading to a light reddish-brown. Attempts to prepare a semicarbazone were quite unsuccessful, and it was found that the further catalytic hydrogenation of the base at 70° could not be accomplished. There was some evidence, in that a weak Liebermann reaction was observed, that the base gives a nitrosoamine, but the isolated product (Found: N, 6·6%) was the unchanged base. Probably the crude material contained a trace of an ester of nitrous acid resulting from the interaction of the acid with the alcoholic hydroxyl group of the base. The *methosulphate* is a readily soluble gum, but the *methiodide* crystallises from alcohol containing a little water in groups of thick, colourless rods, m. p. 320° (decomp.) with darkening from 310° (Found: N, 6·2. $C_{22}H_{27}O_2N_2I$ requires N, 5·9%). It is sparingly soluble in hot alcohol and readily soluble in cold water.

O-*Acetyldihydro*iso*strychnine*.—A mixture of dihydro*iso*strychnine (1 g.), fused sodium acetate (0·5 g.), and acetic anhydride (3·5 c.c.) was heated on the steam-bath for 3 hours. The product was decomposed by water, the acid neutralised by sodium bicarbonate, and the base extracted by chloroform. After removal of the solvent in a vacuum, the residue crystallised from light petroleum, con-

taining a little benzene, in rods which were recrystallised several times from light petroleum without material alteration of the m. p. The slender, colourless needles thus obtained had m. p. 202—204° (Found: C, 72·9; H, 7·1. $C_{23}H_{26}O_3N_2$ requires C, 73·0; H, 6·9%), and m. p. 190—195° when mixed with dihydro*iso*strychnine. O-*Acetyldihydroisostrychnine* is immediately soluble in dilute acetic acid, and on the progressive addition of sodium hydroxide a turbidity appears and then disappears; on keeping, this solution deposits dihydro*iso*strychnine in needles.

Preparation of Dihydrostrychnidine (A).—(I) *By catalytic hydrogenation of strychnidine.* The reduction of strychnidine could not be accomplished at the ordinary temperature, and under the following conditions it gave good results on a small scale only. A violently agitated mixture of norite (4 g., previously heated to redness) and palladous chloride (0·4 g.) dissolved in very dilute hydrochloric acid (100 c.c.) was allowed to absorb hydrogen, and when no further change occurred a solution of strychnidine (3 g.) in 67% acetic acid (30 c.c.) was introduced and the flask immersed in water at 65° (renewed when it cooled to 50°). After 3½ hours the volume of hydrogen absorbed was 190 c.c. (theory, 210 c.c.) and absorption ceased. The base was precipitated from the filtered liquid by means of sodium hydroxide, and the grey granules were collected and dried in a vacuum (yield, 50%; m. p. 200—209°). The substance, crystallised from methyl alcohol and then from light petroleum, formed small, well-defined, colourless tablets, m. p. 212—214° (Found: C, 78·3; H, 7·9. $C_{21}H_{26}ON_2$ requires C, 78·3; H, 8·1%). When crystallised from methyl alcohol the base forms large, glistening, colourless leaflets (Found: C, 78·6; H, 8·0%). *Dihydrostrychnidine* (A) is not appreciably soluble in boiling water, but it is readily soluble in cold ethyl alcohol, benzene, or carbon tetrachloride; it is moderately readily soluble in hot ethyl acetate, and sparingly soluble in boiling acetone and light petroleum. Unlike strychnidine, it gives only a faint coloration when ferric chloride is added to its solution in an excess of dilute hydrochloric acid; a rose-red coloration develops on warming. If only a trace of hydrochloric acid is present, an intense coloration develops a few seconds after the addition of ferric chloride. As explained in Parts IV and V (this vol., pp. 1595, 1662), this behaviour is closely connected with the strength of the substances as di-acid bases, and is a clear indication that the nitrogen atom joined to the aromatic nucleus is a much stronger basic centre in dihydrostrychnidine (A) than it is in strychnidine. The base is stable to potassium permanganate in cold acetone solution containing a few drops of water, but it is rapidly oxidised if much water is added. It is

unaffected by acetic anhydride and dry sodium acetate at 100°. The base is unacted upon by magnesium phenyl bromide in boiling benzene or by magnesium methyl iodide. It was also recovered unchanged after vigorous treatment with sodium and boiling *iso*amyl alcohol.

(II) *By electrolytic reduction of dihydrostrychnine.* Dihydrostrychnine dihydrate (22 g.), dissolved in a mixture of concentrated sulphuric acid (83 c.c.) and water (100 c.c.), was reduced at a lead cathode (compare Tafel, *Annalen*, 1898, **301**, 302) by a current of 6 amps. at 3·8 volts (current density, 0·09 amp./cm.^{2}). At the end of 3 hours, the liquid in the cathode cell gave no appreciable ferric chloride reaction; at the end of 9 hours both the ferric chloride and Otto reactions were positive; after 18 hours the Otto reaction was very faint; and after 2 hours more it had disappeared. Tafel (*loc. cit.*) found that strychnine was completely reduced (using similar conditions, but with a rather smaller current density and a rotating cathode) in 8 hours, so that dihydrostrychnine is apparently less easily reduced by this method than strychnine is. The liquid was diluted with 3 times its volume of water, and the base precipitated by the cautious addition, with cooling, of potassium hydroxide. The crude product was collected and dried (14 g.). After crystallisation from methyl alcohol and then from light petroleum, pure dihydrostrychnidine (A) was obtained, m. p. 212—214°, unchanged by admixture with a specimen obtained as in (I). The above method is the one that should be adopted for the preparation of the base in quantity.

Dihydrostrychnidine (A) *methosulphate* was obtained under conditions similar to those used for dihydrostrychnine methosulphate (p. 2394). It crystallises from alcohol–light petroleum in rosettes of colourless, pointed needles, m. p. 250° (decomp.) (Found: C, 61·3; H, 7·5; N, 5·8. $C_{23}H_{32}O_5N_2S$ requires C, 61·6; H, 7·2; N, 6·2%). The derivative is readily soluble in water and alcohol and sparingly soluble in most other organic solvents. The salt (2 g.) was heated at 105—115° for 8 hours (reflux) with 40% methylalcoholic potassium hydroxide (22 c.c.). On addition of water, fine, colourless leaflets separated. Complete purification was effected by two crystallisations from methyl alcohol, and the massive, colourless, hexagonal tablets, m. p. 219—220°, were found to consist of methoxymethyltetrahydrostrychnidine (Part IV, this vol., p. 1617). The m. p. was not depressed on admixture with a specimen obtained by the electrolytic reduction of methoxymethyldihydrostrychnidine.

The methiodide. Dihydrostrychnidine (A) (5 g.) was suspended in methyl alcohol (50 c.c.), and methyl iodide (12 c.c.) added; the

base then dissolved completely with little rise of temperature, crystallisation soon commenced, and a sandy precipitate separated. The mixture was boiled for ½ hour and left over-night; the *methiodide* was then collected, washed with methyl alcohol, and dried at 100°. When rapidly heated, it decomposed at about 340—350° to a brown syrup. It is sparingly soluble in boiling water or methyl alcohol and separates from water in striated, arrow-shaped prisms (Found: C, 57·0; H, 6·4. $C_{22}H_{29}ON_2I$ requires C, 56·8; H, 6·5%).

The *methochloride* was obtained by digesting the methiodide with much water and silver chloride for 2 hours and evaporating the filtered solution to a small bulk; a colourless syrup remained which, kept over sulphuric acid in a vacuum desiccator, crystallised to a mass of needles. After contact with porous porcelain, the colourless mass was recrystallised from a few drops of water, and dried over sulphuric acid. It did not then lose weight at 100° (Found: C, 70·7; H, 8·0. $C_{22}H_{29}ON_2Cl$ requires C, 70·8; H, 7·9%). This substance decomposes at about 345° and the aqueous solution gives with hydrochloric acid and ferric chloride a pale pink colour, which gradually becomes deep pink on warming. The solution in dilute sulphuric acid (60%) is coloured intensely brownish-crimson by dichromate. The methochloride (0·5 g.) was heated cautiously in a test-tube over a free flame until decomposition at the high temperature was just complete; the residue crystallised from methyl alcohol (norite) in leaflets, m. p. 212—213°, of dihydrostrychnidine (A). When the methochloride was heated with methyl-alcoholic potassium hydroxide (25%) on the sand-bath until the temperature of the melt reached 125°, the resulting product gave on addition of water a grey mass, which was well washed and left in contact with porous porcelain. This separated from xylene (norite) in leaflets, m. p. 220—222°, and proved to be methoxymethyltetrahydrostrychnidine.

As stated in the Addendum at the end of this paper, these and other properties prove that dihydrostrychnidine (A) methiodide and methochloride are identical with methyl*neo*dihydrostrychnidinium iodide and chloride (Part IV, this vol., p. 1623).

The dimethosulphate and dimethiodide. A solution of dihydrostrychnidine (A) (7 g.) in carefully purified boiling benzene (50 c.c.) was cooled, and freshly distilled methyl sulphate (20 c.c.) added; the solution became warm, clouded, and the monomethosulphate separated as a voluminous crystalline precipitate. On heating on the steam-bath under reflux, the crystals gradually gave place to a gelatinous mass. After the mixture had been boiled for 15 hours and cooled in ice-water, the benzene layer was decanted and the viscid dimethosulphate, which showed no sign of crystallising, was

dissolved in water. The solution was filtered from benzene, neutralised with potash, and heated to boiling, and a large excess of hot sodium iodide solution added. The clear solution soon began to deposit brilliant, arrow-shaped plates of the *dimethiodide*, which were collected, washed, and dried at 100°; m. p. about 285—290° (decomp.) (Found: C, 46·0; H, 5·5. $C_{23}H_{32}ON_2I_2$ requires C, 45·6; H, 5·3%). A further small crop of crystals was obtained on concentrating the mother-liquor; the filtrate gave, on addition of 50% potassium hydroxide solution, only a slight turbidity (compare Part IV, this vol., p. 1594).

The same dimethiodide was obtained when dihydrostrychnidine (A) was heated in a sealed tube with a large excess of methyl iodide alone (compare the preparation of the monomethiodide above) for several hours in the steam-bath, since the old-gold plates which separated had m. p. 285—290° (decomp.) and gave C, 45·2; H, 5·5%. This dimethiodide is very sparingly soluble in boiling methyl alcohol, but dissolves readily in cold and very readily in hot water.

The *dimethochloride*, prepared from the dimethiodide and silver chloride in the usual way, is a hygroscopic syrup.

After this had been heated on the sand-bath with methyl-alcoholic potassium hydroxide (25%) in an open flask until the temperature of the melt was 130°, the cold product gave with water a grey precipitate of methoxymethyltetrahydrostrychnidine and *methyldihydrostrychnidine* (A) in about equal proportions. Owing to the small quantity of material available, the separation of these two substances proved to be difficult. The mixture was dissolved in boiling benzene and the solution was digested with norite and concentrated to a very small bulk. On standing in ice, crude methoxymethyltetrahydrostrychnidine separated. After crystallisation from xylene, it melted at m. p. 220—222°, alone or when mixed with a specimen of the methoxy-derivative obtained as described in Part IV (this vol., p. 1617). The benzene filtrate was evaporated, and the colourless syrup boiled with methyl alcohol; a mass of crystals, m. p. 155—190°, then separated. This crude substance was rubbed with a very little benzene, the small quantity of very sparingly soluble residue, m. p. 220—222°, was filtered off, and the syrup was again treated with methyl alcohol after the benzene had been evaporated. This process was repeated and the substance was then crystallised from methyl alcohol and finally from acetone (Found, in two different preparations: C, 79·0, 78·9; H, 8·5, 8·4. $C_{22}H_{28}ON_2$ requires C, 78·6; H, 8·3%).

Methyldihydrostrychnidine (A) melts not quite sharply at 178—180° and is characterised by being remarkably sparingly soluble in

boiling methyl alcohol or acetone and unusually readily soluble in benzene. It separates from methyl alcohol or acetone in flat needles. A solution in dilute hydrochloric acid gives, on treatment with ferric chloride, an immediate crimson colour, changing to pale brown on warming. The base has unexpectedly little tendency to combine with methyl iodide. When a concentrated solution in benzene was boiled with methyl iodide for several minutes and evaporated, the residue obtained consisted essentially of the unchanged base and separated from methyl alcohol in needles, m. p. 175—177° (Found: C, 78·3; H, 8·2%). The base is readily soluble, without rise of temperature, in methyl iodide and even after 10 minutes' boiling a good deal of uncombined base remains.

Hexahydrostrychnine (*Dihydrotetrahydrostrychnine*).—(A) *Catalytic reduction of tetrahydrostrychnine.* This was carried out as in the cases described already, and the quantities were: palladous chloride (0·8 g.), water (300 c.c.), norite (12 g.), tetrahydrostrychnine (6 g.), 50% acetic acid (60 c.c.). Absorption at the ordinary temperature was very slow (20 c.c. in 1 hour), but at 50—70° the theoretical volume of hydrogen was absorbed in 4 hours. The filtered liquid was made strongly alkaline with potassium hydroxide (cooling necessary), and the slightly pink, granular solid was collected and dried in a vacuum (yield, 60%). The *hexahydrostrychnine* crystallises from ethyl acetate, containing a little light petroleum, in large, rectangular tablets, mostly with facets at the corners, and faintly pink as the result of superficial oxidation. The m. p. of this substance, 197—199°, is thus close to that of tetrahydrostrychnine (200—202°), but a mixture of the two gave a very large depression (Found: C, 74·4; H, 8·2. $C_{21}H_{28}O_2N_2$ requires C, 74·1; H, 8·3%). This base is sparingly soluble in light petroleum and appreciably soluble in boiling water; it is moderately readily soluble in cold ethyl acetate and in boiling benzene, acetone, or carbon tetrachloride, and readily soluble in cold ethyl alcohol or boiling methyl alcohol. Like tetrahydrostrychnine, hexahydrostrychnine gives no coloration with ferric chloride if too much hydrochloric acid is present in the solution, but in the presence of only a trace of acid a brownish-red coloration slowly develops.

(B) *By electrolytic reduction of dihydrostrychnine.* The alkaline solution from which crude dihydrostrychnidine was precipitated (see p. 2400) was exhaustively extracted with chloroform, the red extract separated and dried over sodium sulphate (norite), and the solvent removed, finally in a vacuum at 40°. The residual gum solidified in contact with light petroleum, and this material (5 g. from 22 g. of dihydrostrychnine), after three crystallisations from ethyl acetate containing light petroleum, was obtained in large,

faintly brown, irregular tablets, m. p. 197—199°, alone or mixed with the specimen prepared as described under (A) above.

Evidence was obtained that hexahydrostrychnine yields a nitrosoamine, but the substance could not be fully purified. Similarly, the *diacetyl* derivative, prepared in the usual manner (compare *O*-acetyldihydro*iso*strychnine), was obtained only as a very pale yellow, hygroscopic syrup (Found: N, 6·8. $C_{25}H_{32}O_4N_2$ requires N, 6·6%). It is of interest to note that this substance gives no coloration with ferric chloride, thus indicating the neutralised character of the nitrogen atom attached to the aromatic nucleus. The dehydration of hexahydrostrychnine with formation of dihydrostrychnidine (A), analogous to the conversion of tetrahydrostrychnine into strychnidine, can be accomplished by boiling the substance with ten times its weight of phosphoryl chloride for 4 minutes. The crude base, isolated in the usual way, has m. p. 200—210°, and yields pure dihydrostrychnidine (A), m. p. 212—214°, after one crystallisation from light petroleum.

iso*Strychnidine*.—The electrolytic reduction of *iso*strychnine was effected in the usual apparatus. *iso*Strychnine trihydrate (13 g.), dissolved in a cold mixture of concentrated sulphuric acid (50 c.c.) and water (70 c.c.), was placed in the cathode cell and submitted to a current of 4·4 amps. at 4 volts (current density, 0·065 amp./cm.^{2}) for 20 hours, after which the Otto reaction could no longer be obtained. The base precipitated by means of potassium hydroxide from the diluted solution (with cooling) weighed 9 g., and was repeatedly extracted with much boiling water. On cooling, the solutions deposited tufts of slender, very pale brown needles, m. p. 155—157°, with sintering at 107—118°. The behaviour on heating was not altered by subsequent recrystallisation from water (Found: loss at 105°, 6·9; at 130°, 7·4. Found in anhydrous material: C, 78·7; H, 7·6. $C_{21}H_{24}ON_2,1{\cdot}5H_2O$ requires H_2O, 7·8. $C_{21}H_{24}ON_2$ requires C, 78·8; H, 7·5%). iso*Strychnidine* which had been heated at 110° for an hour was crystallised thrice from light petroleum and formed very light, feathery groups of colourless needles, m. p. 163—168° (slight decomp.) [Found: (A) C, 77·6; H, 7·9%]. Again, the alkaline mother-liquors from the crude *iso*strychnidine were worked up by extraction with chloroform in the usual manner, with the object of determining whether any *iso*tetrahydrostrychnine was formed in the reduction, but the only definite product isolated was one that crystallised from light petroleum in colourless needles, m. p. 165—167°, alone or mixed with the specimen of m. p. 163—168° mentioned above (Found: C, 76·5; H, 7·5. $C_{21}H_{24}ON_2,0{\cdot}5H_2O$ requires C, 76·6; H, 7·7%). The analysis (A) (above) requires a still smaller proportion of

associated water (0·25 mol.). *iso*Strychnidine is easily decomposed on heating, *e.g.*, it is discoloured at 110° after 1 hour, and a possible explanation of our results is that the low m. p. of the product crystallised from water is the result of decomposition occurring during the sintering period, when solvent of crystallisation is being removed. Crystallisation from light petroleum seems to give less fully hydrated modifications, which may melt at higher temperatures as the result of their superior stability. Confirmation of this view was obtained by crystallising a specimen, m. p. 163—168°, from water, whereupon the m. p. fell to 155—157°. *iso*Strychnidine is readily soluble in cold methyl and ethyl alcohols, ethyl acetate, acetone, or chloroform, and in boiling benzene, from which a small proportion crystallises on cooling in elongated, rectangular plates. It is sparingly soluble in light petroleum. In the presence of an excess of dilute hydrochloric acid, it gives no coloration with ferric chloride when cold, and a very pale colour on warming. If only a trace of hydrochloric acid is present, an intense rose-red colour develops in a few seconds. The *methosulphate* crystallises from a mixture of alcohol and light petroleum in minute, elongated, rectangular, nearly colourless prisms, m. p. 200—205° (decomp.) (Found: N, 5·9. $C_{23}H_{30}O_5N_2S$ requires N, 6·3%). When heated with methyl-alcoholic potassium hydroxide, it yielded a resinous base that could not be crystallised and was not further investigated.

*Dihydro*iso*strychnidine* (a).—This base was obtained by the electrolytic reduction of dihydro*iso*strychnine. A solution of this (10·1 g.) in a mixture of concentrated sulphuric acid (50 c.c.) and water (80 c.c.) was submitted to a current of 4 amps. (3·7—4·1 volts), the current density at the lead cathode being 0·07 amp./cm.^{2}. The anode cell contained 20% sulphuric acid. At the end of 21 hours the Otto reaction was no longer exhibited, and the *dihydro*-iso*strychnidine* (a) was isolated as a pale yellow, gelatinous precipitate (8 g.), which, crystallised from acetone and then twice from benzene, formed pale yellow bunches of needles, m. p. 191—192°. A final crystallisation from light petroleum (b. p. 80—100°) did not alter the m. p. (Found: C, 76·5, 75·9; H, 8·6, 8·1; *M*, in camphor by micro-Rast, 301. $C_{21}H_{26}ON_2,0·5H_2O$ requires C, 76·1; H, 8·2%; *M*, 331). On being heated at 110° for 8 hours, the substance lost only 1·0% (theory, 2·7%), and this suggested the possibility that it might be an ether derived from two molecules of the hypothetical hexahydro*iso*strychnine. The molecular-weight determination disposes of this view and makes it necessary to assume that the compound is $2C_{21}H_{26}ON_2,H_2O$, giving $C_{21}H_{26}ON_2$ and $C_{21}H_{26}ON_2,H_2O$ in fused camphor solution. Naturally any water set free would be evaporated at the temperature of fused

camphor, and so would not affect the result. The original alkaline mother-liquor, from which this base was collected, was extracted with chloroform, and the gum remaining after removal of the solvent was purified by solution in ethyl acetate and precipitation with light petroleum, followed by two similar processes, using benzene and light petroleum. The product, m. p. 170—190°, then crystallised from water in tiny, colourless leaflets, m. p. 191—192° (Found: C, 75·6; H, 8·1%). This substance was readily soluble in hot water, and was unaltered by further crystallisation. It thus appeared to differ from the specimen first described, but a mixture of the two specimens had m. p. 191—192°. The base from the first precipitate was boiled with 1000 parts of water, which dissolved only 5% of its weight. On evaporation of the solution, nearly colourless leaflets, m. p. 190°, alone or mixed with the original material, were obtained. In all such cases it is very difficult to determine whether we are observing the behaviour of a mixture of isomerides, or whether it is merely an example of the large influence occasionally exerted by traces of impurity on the solubility properties. The base is readily soluble in methyl alcohol, ethyl acetate, or boiling benzene, it is moderately readily soluble in boiling acetone, and sparingly soluble in boiling light petroleum. It exhibited the usual ferric chloride reaction, and was partly recovered unchanged after boiling with phosphoryl chloride and after treatment with nitrous acid.

Dihydroisostrychnidine (b).—Unlike strychnidine, *iso*strychnidine may be catalytically reduced at the ordinary temperature. The quantities employed were: palladous chloride (0·5 g.), dissolved in water (200 c.c.) and a little hydrochloric acid, norite (7 g.), *iso*strychnidine (2·4 g.), dissolved in a little dilute acetic acid. The volume of hydrogen absorbed in 3 hours was 200 c.c. (theory, 160 c.c.). The filtered liquid was basified with sodium hydroxide, and the gelatinous precipitate collected and boiled with water (800 c.c.). On cooling, the filtered solution deposited copiously small, colourless plates, and these crystallised from water in tufts of slender, colourless needles, m. p. 150°. Further extraction of the crude product yielded nothing. The *dihydroisostrychnidine* (b) was twice recrystallised from light petroleum (b. p. 60—80°), giving spongy clusters of colourless needles, m. p. 151—153° after sintering at 140° (Found: C, 73·9; H, 8·2. $C_{21}H_{26}ON_2,H_2O$ requires C, 74·1; H, 8·3%). This material, evidently a monohydrate, lost 3·6% at 110—120° in 4 hours (theory, 5·3%), but some discoloration occurred. The solubilities, except in water, were similar to those of dihydro*iso*strychnidine (a) and the new base gives a rose-red colour on the addition of ferric chloride, even in an excess

of dilute hydrochloric acid. Our examination of the isomeric dihydro*iso*strychnidines is not complete and we have not yet sufficient data to enable us to advance any suggestions as to the structural or stereochemical differences that may exist between them. Attempts to obtain one or other of these compounds from dihydrostrychnidine (A) were fruitless. Dihydrostrychnidine (A) is quite unchanged when it is heated with water at 180—185° for 6½ hours or with methyl-alcoholic ammonia at 120—145° for 48 hours.

Dioxyhydroxydihydrostrychnidine.—Strychnidine was unaffected by heating with methyl-alcoholic ammonia at 130—140° for 48 hours and also by treatment with alcoholic sodium ethoxide under various conditions. When heated with water, it yielded the oxidation product here described, but no *iso*strychnidine. Strychnidine (10 g.) was heated with water (300 c.c.) (and some air) at 170—185° for 5½ hours in a phosphor-bronze autoclave; 5 g. of the base were recovered unchanged, and the aqueous solution was concentrated to one-fourth of its original volume, filtered, and kept in the ice-chest. An abundant crystallisation occurred and the *dioxyhydroxydihydrostrychnidine* was recrystallised several times from water; flat, pointed, colourless needles, m. p. 260° (decomp., darkening from 250°) (Found: loss at 105°, 15·3; N, 6·4. Found in anhydrous material: C, 68·6; H, 7·0. $C_{21}H_{26}O_4N_2,4H_2O$ requires H_2O, 16·3; N, 6·3. $C_{21}H_{26}O_4N_2$ requires C, 68·1; H, 7·0%). The anhydrous substance is hygroscopic and recovers almost the whole of its water of crystallisation on exposure to the air for a week. The base is much more readily soluble in water than any other strychnine derivative (except the salts) described in this memoir; it is also readily soluble in the simple alcohols and in boiling benzene or chloroform, but very sparingly soluble in hot ethyl acetate or light petroleum. The ferric chloride reaction is exhibited well in the presence of a large excess of hydrochloric acid.

Dioxyhydroxyhexahydrostrychnine.—When tetrahydrostrychnine was heated with methyl-alcoholic ammonia at 130—140° for 48 hours, it was recovered entirely unchanged. Tetrahydrostrychnine (11 g.) was heated with water (300 c.c.) in a phosphor-bronze autoclave at 170—185° for 6½ hours. The brownish-yellow liquid was filtered from a little black material, concentrated somewhat, again filtered from a tar, and kept in the ice-chest. Bunches of coarse needles (3 g., m. p. 197—203°) separated, and several recrystallisations from water yielded bunches of large, fibrous, colourless needles, m. p. 201—203° (with effervescence a few degrees higher) (Found: loss at 105°, 9·3. Found in anhydrous material: C, 64·9; H, 6·9;

N, 7·1. $C_{21}H_{28}O_5N_2,2H_2O$ requires H_2O, 8·5. $C_{21}H_{28}O_5N_2$ requires C, 65·0; H, 7·3; N, 7·3%). Neither in the case of this base nor in that of the corresponding compound from strychnidine (see the preceding section) is the formula with two hydrogen atoms less excluded by the analyses. The substance is readily soluble in methyl alcohol, sparingly soluble in cold ethyl alcohol, and very sparingly soluble in boiling benzene, chloroform, ethyl acetate, or acetone. It is moderately readily soluble in cold water, but less soluble than the similar strychnidine derivative. With ferric chloride in presence of much dilute hydrochloric acid, it gives only a faint brown coloration; in presence of a trace of hydrochloric acid, an intense brownish-red colour develops rapidly.

p-*Aminostrychnidine.*—The various derivatives of strychnidine all couple with diazobenzenesulphonic acid in acid solution, giving in the course of time equally intensely-coloured solutions, but the speed of the reaction varies greatly from case to case. In acid solution strychnidine couples much more rapidly than dihydrostrychnidine (A), but in neutral solution the velocities are not very different. We interpret this as due to the increased basic strength of the dihydrostrychnidine (A), and it therefore seems probable that the double bond of strychnidine is not far distant in the molecule from the nitrogen atom that is bound to the aromatic nucleus. *Sulphobenzeneazostrychnidine* is a crimson powder, insoluble in organic solvents. The finely powdered substance (2·6 g.) was added to a solution of hydrated stannous chloride (6·5 g.) in concentrated hydrochloric acid (16 c.c.), and the mixture boiled for a few minutes. It was then cooled, rendered strongly alkaline with sodium hydroxide, and extracted with chloroform. The extracts were dried and evaporated until crystallisation began; much light petroleum was then added. The nearly colourless precipitate crystallised from benzene in microscopic prisms which decompose above 330° (Found: N, 12·4. $C_{21}H_{25}ON_3$ requires N, 12·5%). *Aminostrychnidine* is moderately readily soluble in chloroform, sparingly soluble in hot benzene, and practically insoluble in boiling ethyl acetate or light petroleum. This amine gives, with ferric chloride in hydrochloric acid solution, an eosin-red coloration, quickly fading to yellow; addition of sodium nitrite to an acid solution produces the same colour change, but if the solution is used at once it can be shown to contain a diazonium salt. The product of coupling with β-naphthol and H-acid is violet, and with J-acid red. Diazotised sulphanilic acid and aminostrychnidine give a purple coloration, probably not due to a normal azo-compound since it is discharged by the addition of sodium hydroxide. The most interesting colour reactions of aminostrychnidine are, how-

ever, the following, which show that strychnidine has free *m*- and *p*-positions with respect to the nitrogen atom. When ferric chloride is added to a solution of the base in dilute hydrochloric acid containing hydrogen sulphide, a brownish-reddish-purple colour is produced and the solution exhibits an intense brown fluorescence. Addition of ferric chloride to an acid solution containing dimethylaniline gives a royal-blue colour, doubtless owing to the formation of an indamine of the type of Bindschedler's green. If *m*-tolylenediamine is employed in place of the dimethylaniline, a deep blue coloration is developed, and on warming, the solution becomes intense bluish-eosin-red, and on dilution exhibits a striking greenish-yellow fluorescence.

Sulphobenzeneazomethylstrychnine.—Methylstrychnine (0·75 g.) was dissolved in very dilute acetic acid (200 c.c.) and diazobenzenesulphonic acid (0·85 g., 2·2 mols.) added with stirring. A red oil quickly formed and solidified; this was collected and crystallised from much hot alcohol as a dull brick-red powder (Found: N, 9·7%, showing that only one sulphobenzeneazo-group has been introduced). The *substance* is insoluble in organic solvents with the exception of the simple alcohols; it is moderately soluble in cold water, but a change occurs on boiling, the colour deepens and the solid that separates on cooling is readily soluble in cold acetone.

Strychnic Benzoic Anhydride.—Benzoyl chloride (5 c.c.) was gradually added to a well-agitated solution of strychnic acid (4 g.) in 3% aqueous sodium hydroxide (100 c.c.). The light brown precipitate was collected and crystallised from xylene–light petroleum (b. p. 80—100°) in golden-yellow clusters of minute rods, m. p. 215—218° (Found: C, 73·6, 73·7; H, 6·2, 6·4; N, 6·2, 6·3. $C_{28}H_{28}O_4N_2$ requires C, 73·7; H, 6·2; N, 6·1%). A product requiring less purification, and otherwise identical, is obtained from strychnic acid (6 g.), sodium bicarbonate (14 g.), water (200 c.c.), and benzoyl chloride (8 c.c.). This substance is insoluble in dilute aqueous sodium hydroxide and is *slowly* hydrolysed on boiling the solution; it is also hydrolysed on boiling with water. It is, however, *immediately* hydrolysed by dissolution in cold dilute aqueous acids, even acetic acid, and addition of sodium hydroxide then precipitates strychnine. The behaviour of this compound seems inconsistent with any theory of its nature other than that which we have advanced—the formation of mixed anhydrides in the Schotten–Baumann process has frequently been observed in other cases.

Addendum made on October 3rd, 1927. After the present paper had been set up in proof, the discovery was made that dihydro-

strychnidine (A), m. p. 212—214°, is identical with the substance described in Part IV (this vol., p. 1622) as methyl-ψ-dihydrostrychnidine, $C_{22}H_{28}ON_2$, m. p. 212°. The latter was obtained in very poor yield by the action of heat on the dimethochloride (A) of methoxymethyltetrahydrostrychnidine and it was thought that its formation was due to the following change: $C_{23}H_{32}O_2N_2,2MeCl = C_{22}H_{28}ON_2 + 2MeCl + MeOH$.

It is now clear that a more drastic decomposition must take place and that a $>CH_2$ group also is lost at the high temperature necessary for the change. The identity of the substance thus produced with dihydrostrychnidine (A) was proved by a close comparison of the properties, and also by the m. p. (212—214°) of a mixture, of the two preparations. Moreover the analysis given in Part IV, p. 1622 (Found: C, 78·1; H, 8·0; N, 8·5) agrees rather better with the formula $C_{21}H_{26}ON_2$ (Calc.: C, 78·2; H, 8·1; N, 8·7%) than with the formula $C_{22}H_{28}ON_2$ (Calc.: C, 78·6; H, 8·3; N, 8·3%) suggested at the time, and the same applies to the analyses of the derivatives.

It is also clear that the substance described as methyl*neo*dihydrostrychnidinium iodide (*loc. cit.*, p. 1623), obtained from methoxymethyltetrahydrostrychnidine hydriodide by the action of heat, is in reality dihydrostrychnidine (A) methiodide, and a similar correction must be applied to the corresponding chloride. It is therefore necessary in Part IV, pp. 1596, 1597, 1621, 1622 and 1623, to replace the names methyl-ψ-dihydrostrychnidine by dihydrostrychnidine (A) and methyl*neo*dihydrostrychnidinium iodide (chloride) by dihydrostrychnidine (A) methiodide (methochloride). It is also probable that the substance, m. p. 220—221°, described as methyl-ψ-dihydrobrucidine in Part V of this investigation (this vol., p. 1661) is in reality dihydrobrucidine (A), but the proof of this cannot be supplied until this substance has been obtained by a process similar to that employed in the preparation of dihydrostrychnidine (A). Experiments with this object in view are in progress.

The authors wish to thank the Advisory Council of the Department of Scientific and Industrial Research for a grant which has enabled one of them (A. E. O.) to take part in the investigation.

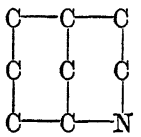
THE UNIVERSITIES OF OXFORD AND MANCHESTER.

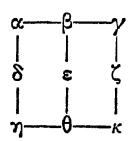
[*Received, July 30th*, 1927.]

CCCXXI.—3-*Hydroxy*cyclo*hexylacetolactone*.

By ROBERT ROBINSON and AHMAD ZAKI.

ACCORDING to Gulland and Robinson (J., 1923, **123**, 980; *Mem. Manchester Phil. Soc.*, 1925, **69**, No. 10), whose suggestions have been amply justified by the important and outstanding experiments of Schöpf (*Annalen*, 1927, **452**, 211), the bases of the morphine group contain the heterocyclic system (I) associated with other rings.

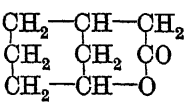
(I.) 

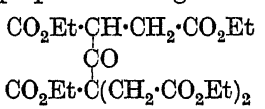


(II.) $\zeta = O$
(III.) $\varepsilon = N$
(IV.) $\beta = \theta = N$
(V.) $\delta = \zeta = N$
(VI.) $\alpha = \gamma = \eta = \kappa = N$

An examination of the literature shows that substances of this type have not been obtained although the similar systems indicated by II, III, IV, V, and VI (where each letter represents a carbon atom except when otherwise specified) are found among synthesised compounds. It is proposed to attempt the synthesis of simple bases of the type (I) in order to examine the degree of stability of the ring structure. Progress in this direction has been made and is reported at this stage because one of us is unable to continue the work.

There is little doubt that the desired base could be obtained from the *lactone* (VII), named in the title, and we have obtained this substance by the reduction of *m*-hydroxyphenylacetic acid with hydrogen in the presence of platinum-black. The yield, however, is poor, the main product being hexahydrophenylacetic acid. It seemed that a better method of preparation might be through

(VII.) 



(VIII.)

3-keto*cyclo*hexylacetic acid, which might be derived by applying the Dieckmann reaction to the ester of methanediacetic-γ-butyric acid, $CH(CH_2\cdot CO_2H)_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$. The latter we hoped to obtain from the tribasic keto-acid which should be the normal product of hydrolysis of the ester (VIII). This has been prepared, but the scheme broke down owing to the wasteful nature of the operations necessary for the introduction of acetic residues into ethyl acetonedicarboxylate.

EXPERIMENTAL.

m-*Hydroxyphenylacetic Acid*.—Anhydro-α-benzamido-*m*-methoxycinnamic acid (35 g.) was hydrolysed as described by Pschorr (*Annalen*, 1912, **391**, 44), but the resulting alkaline solution was

then acidified by the passage of sulphur dioxide, which precipitated the benzoic acid (compare Buck and Perkin, J., 1924, **125**, 1680). After filtration, concentrated hydrochloric acid was added and the solution boiled to expel sulphur dioxide; on cooling, *m*-methoxyphenylpyruvic acid (14 g.) separated (m. p. 154—155° after crystallisation from alcohol). This acid (8·4 g.) was dissolved in 10% sodium hydroxide (70 c.c.), and 3% hydrogen peroxide (50 c.c.) added. After being kept over-night in the cold, the solution was acidified, and *m*-methoxyphenylacetic acid (6 g., m. p. 66—67° after one crystallisation from water) was isolated by means of ether. *m*-Hydroxyphenylacetic acid has been previously obtained by Salkowski (*Ber.*, 1884, **17**, 507) from *m*-nitrophenylacetonitrile by a series of reactions; we have prepared it by demethylation of its methyl ether: *m*-methoxyphenylacetic acid was boiled with 8 times its weight of freshly distilled hydriodic acid (*d* 1·7) for 2 hours. The solution was cooled and diluted with water, free iodine removed by sulphur dioxide, and the acid isolated by ether as a brown oil which gradually crystallised. The product was purified by one crystallisation from benzene, dissolution in aqueous sodium carbonate, successive extraction of the alkaline solution with carbon disulphide and ether, recovery by means of ether, and a final crystallisation from benzene. The acid had the m. p. (129°) and other properties attributed to it by Salkowski (*loc. cit.*).

Catalytic Reduction of m-*Hydroxyphenylacetic Acid.*—A solution of *m*-hydroxyphenylacetic acid (4·5 g.) in acetic acid (20 c.c.) was vigorously stirred with hydrogen in presence of platinum-black (0·7 g.), prepared by Willstätter's method (*Ber.*, 1912, **45**, 1472). After a little time the flask was evacuated and the mixture stirred with air for 10 minutes; on re-evacuation and admission of hydrogen the rate of absorption was found to have been almost quadrupled. In about 12 hours 2330 c.c. of hydrogen had been absorbed. The filtered solution was steam-distilled until about 2000 c.c. of distillate had been collected; the liquid remaining in the flask was then thoroughly extracted with ether, and after removal of the solvent the residue was twice distilled under diminished pressure. The product appeared to be homogeneous, but owing to the small amount available we do not record the b. p. under diminished pressure; under the ordinary pressure, it has b. p. 240—243°, determined by Siwoloboff's method (*Ber.*, 1886, **19**, 795) (Found: C, 69·0; H, 8·5. $C_8H_{12}O_2$ requires C, 68·6; H, 8·6%). This colourless oil is clearly 3-*hydroxy*cyclo*hexylacetolactone*, for it exhibits the behaviour of a lactone: it is immiscible with water, and on the addition of a drop of sodium hydroxide and a trace of phenolphthalein a red coloration is obtained, which soon disappears,

further quantities of sodium hydroxide being similarly slowly neutralised until the whole of the substance has been decomposed. On acidifying and heating the solution, the lactone was regenerated. The distillate from the steam-distillation contained an acid which was isolated by means of ether and distilled. The fraction, b. p. 243—246°, crystallised in the course of 2 days in large, feather-like aggregates, m. p. 30—31° (Found: C, 67·6; H, 10·0. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·8%). From the origin, m. p., analysis, and other properties, there can be no doubt that this substance is identical with hexahydrophenylacetic acid (Wallach, *Annalen*, 1907, **353**, 296). It constituted the main product of the reduction.

Ethyl βδ-*Dicarbethoxy*-γ-*ketopimelate*,

$$CO_2Et{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CO{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et.$$

—An alcoholic solution of sodium ethoxide (from 6·9 g. of sodium) was added during 1½ hours to a mixture of ethyl acetonedicarboxylate (30·3 g.) and ethyl bromoacetate (50 g.), heated on the steam-bath. The mixture was then heated under reflux till neutral, the alcohol distilled, and the product isolated from the residue by means of ether. Thorough drying was found to be essential. The oil was fractionated under 1 mm. pressure, but this process entailed large losses through decomposition. Finally, a homogeneous fraction, b. p. 168—170°/1 mm., was collected (10 g.) (Found: C, 54·8; H, 7·0. $C_{17}H_{26}O_9$ requires C, 54·6; H, 6·9%). Analysis does not determine whether the acetonedicarboxylic ester has been converted into a mono-, di-, tri-, or tetra-substituted derivative, so the ester was hydrolysed by boiling dilute sulphuric acid: acetonediacetic acid, m. p. 142—143° (Volhard, *Annalen*, 1889, **253**, 212) was readily isolated (Found: C, 48·1; H, 6·0. Calc. for $C_7H_{10}O_5$: C, 48·3; H, 5·7%).

Ethyl αββ′-*Tricarbethoxyisobutyrylsuccinate* (VIII).—This substance was obtained from molecular proportions of the foregoing ester (24·7 g.), ethyl bromoacetate, and sodium ethoxide in alcoholic solution. The yield of pure product, b. p. 189—191°/1 mm., was 17 g. (Found: C, 54·8; H, 7·0. $C_{21}H_{32}O_{11}$ requires C, 54·8; H, 6·9%). This would correspond to a 56% yield of the monosubstituted derivative, or a 47% yield of the disubstituted derivative. In view of the amount of recovered material of lower and higher b. p. (10 g. containing at least 2 g. of ethyl bromoacetate) and of the fact that the maximum theoretical yield of disubstituted derivative was 50%, a 47% yield of disubstituted derivative is impossible. The polybasic acid obtained by hydrolysing this ester could not be crystallised.

THE UNIVERSITY, MANCHESTER. [*Received, July 18th*, 1927.]

CCCXXII.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR'N *in Aromatic Substitution. Part VII. The Nitration of Benzphenetidide and of* o-, m-, *and* p-*Nitrobenzphenetidides.*

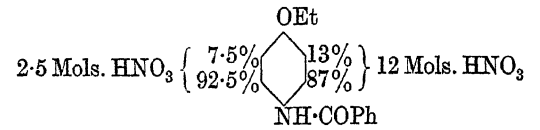
By REGINALD C. FAWCETT and ROBERT ROBINSON.

IN considering the factors governing the relative ease of occurrence of electronic changes, such as those involved in conjugated polarisation, originated or permitted by different atoms, Kermack and Robinson (J., 1922, **121**, 427) suggested two guiding principles: (*a*) that the free electrons in the outer shells are the less active the greater their number; and (*b*) that the activity of free electrons diminishes with increasing atomic weight of the element. Obviously such rules may apply only approximately, and there are alternative ways of stating them, but they serve to correlate experimental results in several fields and give such sequences as NMe_2>SMe>OMe>I>Cl>F for the proton avidity (strength of bases) in the compounds HX and for the effectiveness of the groups in crotenoid systems, and hence for their directive powers in aromatic substitutions of certain types (compare *Chem. and Ind.*, 1925, **44**, 684). The effects of charges, as in the phenoxide and phenylammonium ions, may reverse the order in the series, and this is also true of the effects of substituents which may induce displacements of electrons equivalent to charges. Thus, although the order N>O in aromatic substitution (kationoid reagent, crotenoid system) is theoretically inevitable and justified by everyday laboratory experience so long as we compare neutral, tervalent nitrogen with neutral, bivalent oxygen, yet the application of theory becomes ambiguous when we pass to the comparison of such groups as ·NR·COR and ·OR. Experiment shows that the directive powers of the nitrogenous group can be regulated over a wide range; thus Reverdin (*Ber.*, 1896, **29**, 2595) and Hinsberg (*Annalen*, 1896, **292**, 249) found that the nitration of acet-*p*-anisidide gave acet-3-nitro-*p*-anisidide, establishing beyond question that the directive power of ·NHAc is much greater than that of OMe. Reverdin and Düring (*Ber.*, 1899, **32**, 164) further showed that acet-*o*-phenetidide is changed by nitric acid (41° Beaumé) into its 5-nitro-derivative, although 4-nitro-*o*-phenetidine is obtained by the nitration of *o*-phenetidine in sulphuric acid solution. Similarly the nitration of acet-*o*-anisidide was found to give chiefly the 5-nitro-derivative (Mühlhäuser, *Annalen*, 1881, **207**, 242; Meldola, Woolcott, and Wray, J., 1896, **69**, 1330;

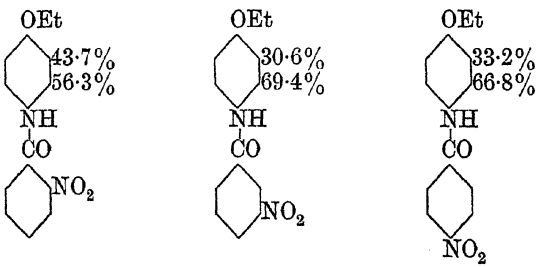
Vermeulen, *Rec. trav. chim.*, 1905, **25**, 12). This has been recently confirmed by Ingold and Ingold (J., 1926, 1310), whose work suggests that owing to the formation of small, undetermined amounts of by-products, the nitration of acet-*o*-anisidide is not a reaction that is suitable for exact quantitative study. On the other hand, Brady, Quick, and Welling (J., 1925, **127**, 2264) found that the nitration of succin-*p*-tolil gave as much as 84% of *N*-2-nitro-*p*-tolylsuccinimide, showing that the group $\cdot N(CO)_2(CH_2)_2$, although itself almost exclusively *p*-directive, is far weaker than methyl in directive power. An explanation, on an electronic basis, of the diminished directive power of nitrogen in such *neutralised* systems (N·CO, etc.) has been already advanced (Robinson, *Chem. and Ind.*, 1925, **44**, 18, 456; Rây and Robinson, J., 1925, **127**, 1618; Part IV, J., 1926, 404; Part V, *ibid.*, p. 411) and may be summarised in the statement that the carbonyl group competes with the aromatic nucleus for the free electrons of the nitrogen octet.

The present investigation is the first of a series in which it is hoped to study the effect of the substituents (R, R') on the directive power of the group R·CO·NR'. In the cases discussed below, R' is H and R is Ph or *o*-, *m*-, or *p*-$NO_2 \cdot C_6H_4$. The circumstance that R' is H involves the possibility of incipient ionisation increasing the directive power or of actual removal of a proton in one of the later phases of the reaction, with the same apparent result. These occurrences should, however, be the more facile the stronger the acid $R \cdot CO_2H$, so they would not influence the directive powers in the sense actually observed, and if taken into account the effects would appear enhanced. The method adopted was to put the groups in turn in competition with ethoxyl, and the reaction examined has been the nitration of the benz-*p*-phenetidides in acetic acid solution at about 0°. Reverdin (*Ber.*, 1911, **44**, 2362) has already studied the nitration of benz-*p*-anisidide and of the isomeric nitrobenz-*p*-anisidides: in each case, the nitrobenzamido-groups were found to be much more powerfully directive than methoxyl, but nothing more than approximately quantitative results were sought. In the present series of experiments, the products were obtained in almost theoretical yield, and thermal analysis showed them to behave as binary mixtures that could contain only traces of other substances. In the case of benz-*p*-phenetidide, the nitration was carried out under two sets of conditions; in the first, nitric acid (2·5 mols.) was gradually added to the phenetidide in acetic acid, and in the second the phenetidide was added to nitric acid (12 mols.) and acetic acid. Thus not only was more acid used in the latter case, but also it was present from the beginning of the operation. The results are

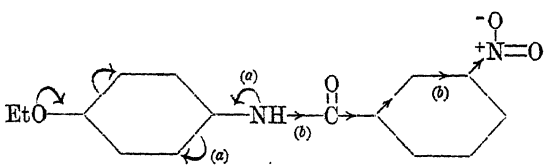
exhibited in the annexed scheme, in which the figures show the proportions in which the nitro-derivatives were formed.



The stronger acid medium has the effect of depressing the directive power of the benzamido-group, and this is clearly due to salt formation and is in harmony with previous experience (compare, *e.g.*, Noelting and Collin, *Ber.*, 1884, **17**, 261; Hollemann, Hartogs, and van der Linden, *Ber.*, 1911, **44**, 704). The nitrobenz-*p*-phenetidides were nitrated under the second set of conditions (12 mols. HNO_3), and as all analogies indicate that these amides should be weaker bases than benz-*p*-phenetidide, the effect of the medium may be expected to be relatively small. The results are expressed graphically thus:

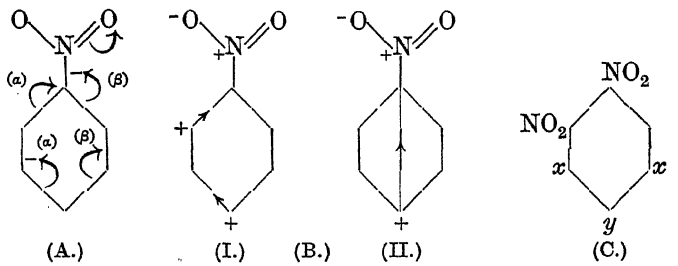


In all three cases, nitration could not be accomplished under the conditions (2·5 mols. HNO_3) that sufficed for the quantitative transformation of benz-*p*-phenetidide, and therefore the general electrical effect of the nitroxyl group makes itself felt over the whole molecule. The figures show, however, that the directive power of the benzamido-group has been diminished to the greater relative extent; the appropriate theory on an electronic basis is represented in the case of the *m*-nitrobenzamido-group by the scheme



in which (*a*) is the directive process and (*b*) is the counteracting general electronic displacement. The effect (*b*) should be more powerful in the *o*- than in the *m*-nitrobenzoyl derivative, and it

should be weakest in the *p*-isomeride. The former deduction is in agreement and the latter in disagreement with the results, which, therefore, suggest that a mechanism exists that enables the more distant group to be the more effective. Such a mechanism may be conjugative (A) or inductive (B) in Kekulé, Dewar, or Claus structures (the last two being regarded as highly improbable and included merely for the sake of completeness), and will also contribute to the enhancement of the effect of an *o*-situated nitroxyl group. In either case, *m*- and *p*-situated nitroxyls induce positive



(A.) (I.) (B.) (II.) (C.)

charges at *x* and *y*, respectively (C). In (A) (β), the conjugation is crotonoid and in (A) (α) it is butadienoid and initiated by the general effect of the nitroxyl; this process is almost indistinguishable from that shown in (B) (I). Oxford and Robinson (Part II, J., 1926, 383) found that the directive powers of the *m*- and *p*-nitrobenzyloxy-groups were identical, and the contrast with the results obtained in the present investigation is probably due to the fact that in the benzamido-compounds there is an unbroken sequence of unsaturated atoms, and the point (C of CO), where the effect can theoretically operate so as to influence the directive power of the group, is nearer to the nitrophenyl group than is the corresponding point (O of $Ar{\cdot}O{\cdot}CH_2$) in the nitrobenzyloxy-compounds. We have examined mathematically the question as to whether a *direct* general effect of the dipole, NO, could give the sequence $o>p>m$, on the theory that in its average position in space a line can be drawn through the centre of the hexagon (benzene ring) and the nitrogen and oxygen atoms. On this stereochemical basis, the disparity between the anticipated effects from the *m*- and *p*-positions is reduced by reason of the oblique orientation of the dipole couple in the *m*-position, but on every probable assumption in regard to the relative distances (nuclear C to N, N to O, nuclear C to a point X, where the effect is operative across the intervening space to the couple N—O) we find $o>m>p$ for the resultant field (at X in the direction of the centre of the nucleus) of the dipole. Taking dynamic conditions into consideration, *e.g.*, free revolution of the nitroxyl group and other

ambiguities, it cannot yet be concluded, however, that an explanation of the order $o>p>m$ is impossible on purely stereochemical lines. It is proposed to extend the investigation with the help of an experimental model.

Finally, a point raised by Orton and Bradfield (this vol., p. 986) in connexion with the directive power of the benzamido-group may be mentioned. These authors have found that the velocity of chlorination of benzanilide exceeds that of acetanilide, which indicates that the directive power of benzamido- is greater than that of acetamido-. (In passing, it may be remarked that Brady, Quick, and Welling, *loc. cit.*, found that phthalimido- had a somewhat greater directive power than succinimido-, providing further evidence in the same direction.) The inconsistency of this result on our electronic basis with the fact that benzoic acid is stronger than acetic acid was commented on. Kermack and Robinson (*loc. cit.*) suggested, however, that the aromatic nucleus is a resonator, being either key-negative or key-positive, according to circumstances. It should be regarded as subservient, in a measure, to the needs of other groups, and ready in some phases to supply electrons, in others to accept them. A further generally applicable conception is that when phases leading to activation and phases leading to inhibition of some particular process or reaction alternate, then the activation phases assume by far the greater importance in producing the observed results. In benzoyl derivatives, there will be phases in which the electron density in the neighbourhood of the carbonyl group is increased (retardation of ionisation of benzoic acid, but acceleration of substitution in benzanilide), and other phases in which it is relatively decreased (acceleration of ionisation of benzoic acid, but retardation of substitution in benzanilide).

EXPERIMENTAL.

2-Nitro-4-aminophenetole sulphate was obtained in 50% yield by Reverdin's method (*Helv. Chim. Acta*, 1927, **10**, 3). 3-Nitro-4-aminophenetole was prepared from phenacetin (40 g.) by the method described in D.R.-PP. 99338 and 38322; the yield of product, m. p. 112·7—113·2°, was 37·5 g.

2-*Nitro*-4-*benzamidophenetole*, (A).—2-Nitro-4-aminophenetole sulphate (10 g.) was added to pyridine (200 c.c.), and benzoyl chloride (10 g.) gradually introduced with vigorous shaking. After 1 hour water was slowly added and the precipitated solid was collected; it crystallised from methyl alcohol (charcoal) in flat, yellow needles, m. p. 149—150° (Found: C, 62·8; H, 5·0. $C_{15}H_{14}O_4N_2$ requires C, 62·9; H, 4·9%).

3-*Nitro*-4-*benzamidophenetole*, (B).—3-Nitro-4-aminophenetole (10

g.) was similarly benzoylated by means of benzoyl chloride (15 g.) in pyridine (150 c.c.); the product crystallised from alcohol (charcoal) in tufts of slender, orange needles, m. p. 121·5—122° (Found: C, 63·0; H, 5·1%).

Mixtures of the Isomerides (A) *and* (B).—The freezing points were determined with the usual precautions, first approximately and then more accurately, the outer bath being kept at such a temperature as to maintain the tube containing the material at 1—2° below the freezing point. The mixture was then heated to 15—20° above the m. p. and allowed to cool after the tube was replaced in the air-jacket. Vigorous stirring was practised at 1—2° above the f. p., and slower but steady stirring in the neighbourhood of the f. p. Several concordant results were obtained for each mixture, and all values were rejected when the degree of supercooling exceeded 0·5—1°. All the graphs constructed were smooth, two-branched curves.

The following f. p.'s were determined:

By adding (A) *to* (B).

% (B)	100·0	95·1	89·8	84·3	78·1	72·4	64·8
F. p.	120·2°	118·2°	116·2°	114·2°	111·95°	109·6°	106·2°

By adding (B) *to* (A).

% (B)	41·7	35·4	33·6	26·5	20·5	13·5	6·4	0·0
F. p.	124·5°	128·1°	129·1°	134·2°	137·4°	141·1°	144·8°	147·75°

*Nitration of Benz-*p*-phenetidide.*—Benz-*p*-phenetidide, prepared by the Schotten–Baumann method, crystallised from alcohol in glistening, white laminæ, m. p. 174·5—175°.

(1) *Nitration with* 2·5 *mols. of nitric acid.* A mixture of boiled nitric acid (*d* 1·41; 5 c.c.) and pure acetic acid (12·5 c.c.) was added in the course of ½ hour to benz-*p*-phenetidide (5 g.) suspended in acetic acid (125 c.c.), the vessel being surrounded by melting ice. The highest temperature recorded was 3°. After 1·5 hours, the product was precipitated by water, collected, washed, and dried (5·85 g. or 98·7%) (Found: C, 62·6; H, 4·9. Calc.: C, 62·9; H, 4·9%). This material had f. p. 117·3°, corresponding, from the graph, with a mixture (*a*) containing 92·5% of the isomeride (B), or to a second composition excluded by the confirmatory tests. A mixture of the nitration product (0·8222 g.) and (A) (0·1315 g.) should therefore contain 79·75% of (B): actually, it had f. p. 112·5°, corresponding with 79·8% of (B). The further addition of (A) (1·1502 g.) to this mixture gave a product of f. p. 128·0°, corresponding to 36·5% of (B) [Calc. from (*a*): 36·1% of (B)].

(2) *Nitration with* 12 *mols. of nitric acid.* Benz-*p*-phenetidide (2 g.) was added to a mixture of boiled nitric acid (10 c.c., *d* 1·41) and

acetic acid (40 c.c.) cooled in melting ice; after 10 minutes' stirring, water (400 c.c.) was added, stirring continued for 15 minutes, and the product isolated (2·35 g., or 99·0%) (Found: C, 63·0; H, 5·0%). The following results were obtained on thermal analysis.

Mixture taken, g.	Isomeride added, g.	F. p.	Composition, % (B): From graph.	Calc. from (*b*).
1·1836	—	115·2°	87 (*b*)	—
1·1836	1·2481 (B)	117·7	93·2	93·3
0·3823	0·8056 (A)	132·6	28·5	28·0

2-*Nitro*-4-o-*nitrobenzamidophenetole*, (C), prepared by the pyridine method, crystallised from methyl alcohol (charcoal) in pale yellowish-green, nacreous plates, m. p. 165—166° (Found: C, 54·5; H, 4·1; N, 12·9. $C_{15}H_{13}O_6N_3$ requires C, 54·4; H, 3·9; N, 12·7%). On exposure to light the crystals become pink. 3-*Nitro*-4-o-*nitrobenzamidophenetole*, (D), obtained similarly in 70% yield, crystallised from methyl alcohol (charcoal) in colourless, prismatic needles, m. p. 131—131·5° (Found: C, 54·2; H, 4·0%).

Mixtures of the Isomerides (C) *and* (D).—

By adding (C) *to* (D).

% (D)	100·0	94·5	87·05	82·5	76·1	69·5	63·8
F. p.	129·7°	126·7°	122·6°	119·9°	116·1°	112·6°	112·6°

By adding (D) *to* (C).

% (D)	40·4	32·9	28·1	22·3	17·1	5·4	0·0
F. p.	138·2°	144·0°	146·9°	150·3°	153·8°	161·0°	164·3°

Nitration of o-*Nitrobenz*-p-*phenetidide*.—The phenetidide (11·8 g.) was derived from *p*-phenetidine (9 g.) and *o*-nitrobenzoyl chloride (12 g.) in pyridine (100 c.c.) solution; it crystallised from methyl alcohol (charcoal) in long, silky, white needles, m. p. 170—171° (Found: C, 62·9; H, 5·1. $C_{15}H_{14}O_4N_2$ requires C, 62·9; H, 4·9%).

o-Nitrobenz-*p*-phenetidide (2·25 g.) was added to a mixture of boiled nitric acid (10 c.c.; *d* 1·41) and acetic acid (40 c.c.), cooled in melting ice, and stirred for 1 hour; the temperature did not rise above 3°. The product was isolated (2·55 g., or 97·9%) (Found: C, 54·2; H, 4·0%). The f. p. of this material was in a neighbourhood in which the determinations of f. p. were somewhat unsatisfactory. The nitration product (0·8397 g.) mixed with (D) (0·8366 g.) had f. p. 117·2°, corresponding with 78% of (D), and hence the original product contained 56·1% of (D). The nitration product (0·3856 g.) mixed with (C) (0·3977 g.) had f. p. 147·2°, corresponding with 27·8% of (D), and hence had initially contained 56·5% of (D).

2-*Nitro*-4-m-*nitrobenzamidophenetole*, (E), obtained in the usual

manner, crystallised from ethyl acetate in matted, hair-like, lemon-yellow needles, m. p. 202—203° (Found: C, 54·4; H, 4·3. $C_{15}H_{13}O_6N_3$ requires C, 54·4; H, 3·9%). The isomeric 3-*nitro*-4-m-*nitrobenzamidophenetole*, (F), crystallised from alcohol in long, silky, golden needles, m. p. 157·5—158° (Found: C, 54·3; H, 4·0%).

Mixtures of the Isomerides (E) *and* (F).—

By adding (E) *to* (F).

% (F)	100·0	93·0	89·2	82·2	80·8	73·0
F. p.	157·4°	153·7°	151·6°	147·9°	147·1°	143·0°

By adding (F) *to* (E).

% (F)	67·0	60·6	52·2	47·4	41·25	34·5	26·3	9·3	0·0
F. p.	152·5°	161·6°	168·9°	172·4°	177·2°	182·4°	187·0°	197·2°	201·6°

Nitration of m-*Nitrobenz*-p-*phenetidide*.—The *m*-nitrobenzoylation of *p*-phenetidine (5 g.) in pyridine solution gave the phenetidide, which crystallised from alcohol in pale yellow needles (7·2 g.), m. p. 163·5—164° (Found: C, 63·1; H, 4·7. $C_{15}H_{14}O_4N_2$ requires C, 62·9; H, 4·9%). The nitration (of 2 g.) was carried out like that of the *o*-nitrobenz-*p*-phenetidide and the yield was 2·30 g. (99·4%) (Found: C, 54·4; H, 4·0; N, 12·9. Calc.: C, 54·4; H, 3·9; N, 12·7%). This crude product was stirred at 18° for 3 hours with methyl alcohol (40 c.c.), then collected, washed with methyl alcohol (10 c.c.), and dried (loss in weight in the process, 0·05 g.). In order to determine whether this washing produced a change in composition, a mixture of (E) (1·0 g.) and (F) (1·0 g.) was treated in exactly the same manner; the recovered material (1·94 g.) had f. p. 170·5°, corresponding to 50% of (F), so the alcohol had dissolved 0·03 g. of each isomeride. The washed nitration product had f. p. 146·0°, corresponding with 78·7% or 70·5% of (F). The nitration product (0·9583 g.) mixed with (F) (1·2589 g.) had f. p. 150·4°, corresponding to 87·0% of (F), and hence the initial content of (F) was 70%. A mixture of the nitration product (0·6811 g.) and (E) (0·6904 g.) froze at 182·4°, corresponding to 34·5% of (F), and hence the original product contained 69·5% of (F). Taking the mean, 70·0% of (F), and correcting for the solubility in methyl alcohol, we find that the crude nitration product contained 69·4% of (F).

2-*Nitro*-4-p-*nitrobenzamidophenetole*, (G), crystallised from alcohol in yellow needles, m. p. 208·5—209·5° (Found: C, 54·4; H, 3·9. $C_{15}H_{13}O_6N_3$ requires C, 54·4; H, 3·9%). 3-*Nitro*-4-p-*nitrobenzamidophenetole*, (H), crystallised from alcohol in flat, glistening, orange needles, m. p. 183·5—184·5° (Found: C, 54·5; H, 4·1%).

Mixtures of the Isomerides (G) *and* (H).—

By adding (G) *to* (H).

% (H)	100·0	95·5	89·9	82·3	74·3	69·3	62·7	58·1
F. p.	183·4°	181·2°	178·8°	175·3°	171·4°	169·0°	165·2°	*ca.* 167°

By adding (H) *to* (G).

% (H)	35·8	28·9	23·1	18·9	11·9	9·4	5·5	0·0
F. p.	185·9°	190·4°	194·0°	196·0°	200·2°	201·6°	203·9°	207·2°

Nitration of p-*Nitrobenz*-p-*phenetidide*.—The phenetidide crystallised from methyl alcohol in flat, pale yellow needles, m. p. 189—190° (Found: C, 63·0; H, 4·9. $C_{15}H_{14}O_4N_2$ requires C, 62·9; H, 4·9%). *p*-Nitrobenz-*p*-phenetidide (4 g.) was nitrated at 0° during 1 hour by means of a mixture of boiled nitric acid (20 c.c.; *d* 1·41) and acetic acid (80 c.c.). The product (yield, 99·6%) (Found: C, 54·4; H, 3·9; N, 13·0. Calc.: C, 54·4; H, 3·9; N, 12·7%) was washed with methyl alcohol, exactly as described above for the *m*-nitrobenznitrophenetidides, and 2·31 g. gave 2·20 g. of the dried, washed material. A mixture of (G) (1·0 g.) and (H) (1·0 g.) was washed in the standard manner and gave 1·90 g. of material, f. p. 174·5°, corresponding to 49·0% of (H); hence the methyl alcohol dissolved 0·03 g. of (G) and 0·07 g. of (H). The following results were obtained on analysis of the washed nitration product.

Mixture taken, g.	Isomeride added, g.	F. p.	Composition, % (H): From graph.	Calc. from (*c*).
1·0005	—	168·3°	68·5 (*c*)	—
1·0005	0·1249 (H)	170·2	72·1	72·0
0·9310	0·8504 (G)	185·3	36·7	35·8

After correction for the methyl alcohol washing, the crude nitration product is found to have contained 66·8% of (H).

Attempts were made to carry out a series of nitrations of the nitrobenzphenetidides in 60% aqueous nitric acid, but, owing to the fact that the nitro-derivatives covered the surface of the crystals, quantitative mono-nitration could not be secured.

We are indebted to the Department of Scientific and Industrial Research for grants which enabled one of us to take part in the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, August 23rd*, 1927.]

CCCXXIII.—*Some Sulphur Derivatives of Substituted Benzaldehydes.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

PREVIOUS work on the mercaptobenzaldehydes appears to be limited to that of Friedländer and Lenk (*Ber.*, 1912, **45**, 2083), who prepared the *o*- and *p*-mercaptans and *o*- and *p*-thioethers of benzaldehyde itself. The present paper records the preparation of several substituted benzaldehydes containing sulphur, some of which exhibit remarkable properties.

The *dioxime* of 3 : 3′-*dinitrodibenzaldehyde* 4 : 4′-*disulphide* is a very stable yellow product which, unlike the corresponding 6 : 6′-*disulphide dioxime*, is converted by cold aqueous sodium hydroxide into what appears to be an isomeride of deeper shade, melting 30° lower, and decomposing with violence when heated rapidly, thereby resembling the second dioxime above. The conversion is accompanied by a gradual and remarkable series of colour changes.

Amino-derivatives of the benzaldehyde thioethers proved to be unstable, thus resembling the simple aminobenzaldehydes, although their solutions in acids may be diazotised normally.

The p-*nitrophenylhydrazones* of 3-*chloro*-4- and -6-*methylthiolbenzaldehyde* were scarlet and orange, respectively, and gave bluish-purple and reddish-purple colorations with alkaline hydroxides, thus showing the much more pronounced bathochromic effect of the methylthiol group when para than when ortho to the hydrazine group (compare the azo-group, Hodgson and Handley, J., 1926, 542).

Bromine displaces the methylthiol group from 3-*amino*-6-*methylthiolbenzaldoxime*, forming 2 : 4 : 5 : 6-*tetrabromo*-3-*aminobenzaldoxime*, but it decomposes the 4-methylthiol isomeride.

EXPERIMENTAL.

3 : 3′-*Dinitrodibenzaldehyde* 6 : 6′-*Disulphide*.—This was prepared by gradually adding aqueous sodium disulphide (crystallised sodium sulphide, 48 g.; sulphur, 6 g.; water, 120 c.c.) to a solution in alcohol (300 c.c.) of 6-chloro-3-nitrobenzaldehyde (64 g.), and boiling for 2 hours; the *disulphide* separated quantitatively as a microcrystalline orange-brown powder, m. p. 230—234° (Found: N, 7·5; S, 20·5. $C_{14}H_8O_6N_2S_2$ requires N, 7·7; S, 17·6%); yield, 60 g. By extracting the crude product (10 g.) with boiling glacial acetic acid (two portions of 100 c.c.) its m. p. could be raised to 257° (8 g.) (Found: N, 7·5; S, 17·6%), and the first extract deposited on cooling a mixture of two kinds of crystals (0·7 g.) which were mechanically separated and proved to be sulphur and a

substance of m. p. 220°; this appears to be a mixture containing mainly the monosulphide (Found: N, 8·5; S, 12·2. Calc.: N, 8·4; S, 9·6%). The second extract also deposited this product, m. p. 220°. The first extract on dilution with water gave a pale straw-coloured substance (0·7 g.), m. p. 207—210° (Found: N, 8·0; S, 14·6%), probably impure monosulphide.

Dioxime. The disulphide (3·5 g.), suspended in alcohol (60 c.c.), was boiled under reflux for 1 hour during the gradual addition of a solution of hydroxylamine hydrochloride (1·6 g.) and sodium acetate (2·6 g.) in water (5 c.c.)—longer boiling produced an inferior product. The hot mixture was filtered, the residue extracted with hot alcohol, and the extract added to the filtrate. The *dioxime* separates from alcohol as a straw-coloured microcrystalline powder which does not melt but decomposes violently between 140° and 160° (yield, 50%) (Found: N, 14·0; S, 16·5. $C_{14}H_{10}O_6N_4S_2$ requires N, 14·2; S, 16·2%); it is insoluble in ether, but moderately soluble in acetic acid.

Di-p-nitrophenylhydrazone. The disulphide (0·36 g.), dissolved in hot glacial acetic acid (100 c.c.), was treated at 50—60° with a solution of *p*-nitrophenylhydrazine (0·36 g.) in glacial acetic acid (5 c.c.); the hydrazone was deposited very gradually, although quantitatively, as red micro-needles, m. p. 283—284° (decomp.) (Found: S, 9·8. $C_{26}H_{18}O_8N_8S_2$ requires S, 10·1%). Alkalis give an immediate reddish-purple colour.

3 : 3′-*Dinitrodibenzaldehyde* 4 : 4′-*Disulphide.*—This is prepared almost quantitatively as above from 4-chloro-3-nitrobenzaldehyde. The crude product is practically pure (m. p. 228—232°), and crystallises from glacial acetic acid in bright yellow needles, m. p. 237—238° (Found: N, 7·8; S, 17·7. $C_{14}H_8O_6N_2S_2$ requires N, 7·7; S, 17·6%).

Dioxime. Oximation as described above was complete in 15 minutes, as shown by the entire solubility of the product in aqueous sodium hydroxide. It is very sparingly soluble in all the usual solvents and crystallises from glacial acetic acid in fine, yellow needles, m. p. 260—261° (Found: N, 14·1; S, 16·3. $C_{14}H_{10}O_6N_4S_2$ requires N, 14·2; S, 16·2%).

Behaviour towards Aqueous Sodium Hydroxide.—The yellow solution of this dioxime in cold aqueous sodium hydroxide undergoes the following sequence of colour changes during 15—30 minutes: yellow, yellowish-green, olive-green, deep green, reddish-green, red. When the alkali is added to a hot aqueous suspension of the dioxime, the initial deep green colour rapidly turns to red. On acidification of the red solution with acetic or hydrochloric acid, a substance is precipitated (? isomeric dioxime) which possesses a

deeper yellow colour than the original and is more soluble in acetic acid, acetone, or methyl or ethyl alcohol. This product separates from alcohol in crystalline clusters, m. p. 230—232° (decomp.; shrinking at 160—170°) (Found: N, 14·0; S, 15·9. $C_{14}H_{10}O_6N_4S_2$ requires N, 14·2; S, 16·2%). The change at 160—170° increases in violence with the rate of heating, and becomes explosive if the m.-p. tube is plunged in a bath at 170°. Probably this more labile substance is in a similar physical state to the dioxime of 3 : 3′-dinitrodibenzaldehyde 6 : 6′-disulphide above.

Di-p-*nitrophenylhydrazone.* This may be prepared as above, except that the disulphide is dissolved in only 30 c.c. of glacial acetic acid. The product separates immediately as a fine, orange-red, microcrystalline powder, m. p. 305—310° (decomp.) (Found: S, 10·0. $C_{26}H_{18}O_8N_8S_2$ requires S, 10·1%); it gives a claret colour with alkalis.

Preparation of Thioethers from the Disulphides.

3-*Nitro*-6-*methylthiolbenzaldehyde.*—The corresponding disulphide (10 g., m. p. 257°), suspended in alcohol (50 c.c.), was treated gradually with a solution of sodium hydroxide (12 g.) and crystallised sodium sulphide (5 g.) in water (60 c.c.). Dissolution rapidly ensued with rise of temperature, and after the dark red mixture had been kept at 50—60° for 15 minutes, it was cooled, diluted with water (100 c.c.), and vigorously stirred with methyl sulphate (10 c.c.). The granular product (8·8 g.) was extracted with hot 60% acetic acid and left a very sparingly soluble product (this contained an aldehyde group, but has not been identified). The 3-*nitro*-6-*methylthiolbenzaldehyde* was precipitated by dilution of the acetic acid extract, and on recrystallisation from this acid it separated in pale straw-coloured needles, m. p. 159—160° (Found: N, 7·2; S, 16·3. $C_8H_7O_3NS$ requires N, 7·1; S, 16·2%). The by-product was always obtained in spite of many attempts to prevent its formation under different conditions; its production was minimised by the vigorous agitation.

The *oxime* crystallises from alcohol in colourless needles, m. p. 187° (Found: N, 13·4; S, 15·2. $C_8H_8O_3N_2S$ requires N, 13·2; S, 15·1%), and forms a pale yellow, sparingly soluble *sodium* salt. The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in reddish-orange needles, m. p. 250—252° (Found: S, 9·8. $C_{14}H_{12}O_4N_4S$ requires S, 9·6%), and gives a claret colour with alkalis.

3-*Nitro*-4-*methylthiolbenzaldehyde.*—When 3 : 3′-dinitrodibenzaldehyde 4 : 4′-disulphide is reduced by the above procedure, it is essential that the time and temperature of reduction be rigidly

adhered to; methylation then gives a bright yellow, flocculent precipitate, which is very difficult to filter off and dry; dilution of the reaction mixture with three times its volume of water, however, facilitates the filtration (yield, 92%). Extraction with 60% acetic acid leaves almost pure *3-nitro-4-methylthiolbenzaldehyde*, which crystallises from dilute acetic acid in yellow plates, m. p. 141—142° (Found: N, 7·3; S, 16·0. $C_8H_7O_3NS$ requires N, 7·1; S, 16·2%).

The acetic acid extract contained in addition to the above product a non-aldehydic substance which was separated by oximation as follows: The crude product (10 g.), suspended in alcohol (60 c.c.), was boiled for 2 hours under reflux with a solution of hydroxylamine hydrochloride (3·5 g.) and sodium acetate (6 g.) in water (5 c.c.); the mixture was diluted with water (100 c.c.), made alkaline with sodium hydroxide, and heated to 50°, whereby about 70% dissolved. On acidification of the filtered solution, *3-nitro-4-methylthiolbenzaldoxime* was precipitated; it crystallised from alcohol in yellow needles, m. p. 210° (Found: N, 13·5; S, 15·2. $C_8H_8O_3N_2S$ requires N, 13·3; S, 15·1%). This product was totally insoluble in water, only sparingly soluble in the usual solvents, and formed an orange *sodium* salt which gave a red solution in water. *3-Nitro-4-methylthiolbenzaldehyde*-p-*nitrophenylhydrazone* crystallises from glacial acetic acid as an orange, microcrystalline powder, m. p. 294—296° (decomp.) (Found: S, 9·7. $C_{14}H_{12}O_4N_4S$ requires S, 9·6%), and gives a claret colour with alkalis.

3-Nitroso-4-methylthiolbenzyl Alcohol (?).—The residue (3 g.) from the foregoing oximation separation crystallises from hot water in orange-yellow needles, m. p. 127°, and is moderately soluble in the usual solvents. The colours given with concentrated sulphuric acid and alcoholic potassium hydroxide are light cherry-red and deep reddish-orange, respectively, in contrast to the deep red and pale yellow given by 3-nitro-4-methylthiolbenzaldehyde. The product forms neither an oxime nor a *p*-nitrophenylhydrazone; it does not respond to Liebermann's nitrosoamine reaction, but when heated with hydriodic acid (*d* 1·7) it gives methyl iodide and a mercaptan. Further, it only gradually gives a silver mirror when warmed with ammoniacal silver nitrate, and is, in general, a less active reducing agent than the above thioether (Found: C, 52·2, 52·3, 52·3; H, 5·31, 5·26, 5·25; N, 7·72, 7·76, 7·7; S, 17·3, 17·3, 17·4; *M*, cryoscopic in naphthalene, 182, 182. $C_8H_9O_2NS$ requires C, 52·4; H, 4·9; N, 7·65; S, 17·4%; *M*, 183). On reduction with titanous sulphate, only 3 atoms of hydrogen were used, but 3-nitro-4-methylthiolbenzaldehyde consumed only 5 atoms instead of the anticipated 6. The data agree with those required for 3-nitroso-

4-methylthiolbenzyl alcohol, but this constitution is only tentatively adopted.

Reduction of the Nitrobenzaldehyde Thioethers and Preparation of the Chlorobenzaldehyde Thioethers.—The thioether (5 g.), suspended in water (80 c.c.), was reduced by adding sodium hyposulphite (18 g.) all at once (about 1 g. of an insoluble complex by-product was invariably formed). The resulting aminobenzaldehyde thioether could be precipitated by alkalis, but was almost unfilterable and resinified rapidly on keeping (compare *m*-aminobenzaldehyde); the reaction mixture was therefore acidified at 0—10° with hydrochloric acid, diazotised by solid nitrite (12 g.), and decomposed in the usual way with cuprous chloride, the chloro-compound being removed by distillation with steam.

3-*Chloro*-6-*methylthiolbenzaldehyde* is readily soluble in the usual solvents and crystallises from alcohol in colourless cubes, m. p. 65° (Found: Cl, 19·1. C_8H_7OClS requires Cl, 19·0%); yield, 1·6 g. Its *oxime* crystallises from alcohol in colourless needles, m. p. 114° (Found: Cl, 17·5. C_8H_8ONClS requires Cl, 17·6%), and its p-*nitrophenylhydrazone* from glacial acetic acid in orange needles, m. p. 246°, giving a reddish-purple colour with alkalis.

3-*Chloro*-4-*methylthiolbenzaldehyde* was obtained in much smaller yield than its isomeride, and was not so readily volatile in steam. It is soluble in the usual solvents and crystallises from alcohol in colourless needles, m. p. 58—59° (Found: Cl, 18·9%). Its *oxime* crystallises from alcohol in colourless needles, m. p. 134° (Found: Cl, 17·6%), and the p-*nitrophenylhydrazone* from glacial acetic acid in scarlet micro-needles, m. p. 222—223°, which give a bluish-purple colour with alkalis.

Reduction of the Oximes of 3-*Nitro*-4- *and* -6-*methylthiolbenzaldehyde.*—The oxime (2 g.), dissolved in 20% aqueous sodium hydroxide (4 c.c.), was added to a boiling solution of ferrous sulphate (18 g.; crystallised) in water (100 c.c.); ammonia was added periodically and the boiling continued for 1 hour. The hot mixture was filtered, and the aminomethylthiolbenzaldoxime separated in colourless needles on cooling; yield, 80%.

3-*Amino*-6-*methylthiolbenzaldoxime*, m. p. 140° (Found: N, 15·5. $C_8H_{10}ON_2S$ requires N, 15·4%), was treated with bromine water in hydrochloric acid solution at 0°, whereupon 2 : 4 : 5 : 6-*tetrabromo*-3-*aminobenzaldoxime* was formed; it crystallised in colourless needles, m. p. 202—203° (Found: Br, 70·0. $C_7H_4ON_2Br_4$ requires Br, 70·8%), from glacial acetic acid. This product contains no sulphur, is soluble in alkalis, and diazotises in concentrated sulphuric acid solution; the diluted diazo-solution couples with alkaline β-naphthol.

3-*Amino*-4-*methylthiolbenzaldoxime*, m. p. 100° (Found: N, 15·3%), is decomposed by bromine into a tarry complex substance insoluble in alkalis.

Analytical Note.—Estimations of sulphur by the Carius method in products containing the methylthiol group were without exception too low, but the oxidation method with sodium peroxide proved satisfactory.

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, April 14th*, 1927. *Revised, August 9th*, 1927.]

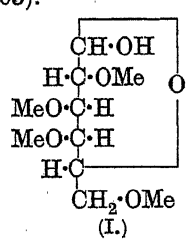
CCCXXIV.—*The Ring Structure in Normal Galactose. Oxidation of Tetramethyl δ-Galactonolactone.*

By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and DAVID IDRIS JONES.

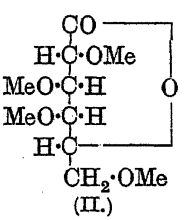
THE form of galactose present in α- and β-methylgalactosides, lactose, raffinose, and melibiose is recognisable as the form which appears in crystalline tetramethyl galactose (Haworth and Long, this vol., p. 544; Charlton, Haworth, and Hickinbottom, *ibid.*, p. 1527; compare Schlubach and Moog, *Ber.*, 1923, **56**, 1957). This compound is readily characterised by its physical properties and by its crystalline anilide. Its oxidation to tetramethyl δ-galactonolactone has also been described (Haworth, Ruell, and Westgarth, J., 1924, **125**, 2468). In the present series of experiments, this lactone has again been examined and the characteristic crystalline *phenylhydrazide* (m. p. 135—137°) of the corresponding tetramethyl galactonic acid has been prepared. From the latter compound the lactone can readily be regenerated and the purified product obtained in this way has properties which are indistinguishable from those previously recorded. The oxidation of this lactone was conducted with nitric acid (*d* 1·42), and from this treatment a liquid product resulted which was isolated in the form of the methyl ester. That this consisted almost entirely of methyl *l*-arabotrimethoxyglutarate was shown by its conversion into the crystalline amide and methylamide. The degradative oxidation of the original sugar was thus carried out in two stages, involving first the oxidation to the lactone by bromine water, and secondly its conversion into a dibasic acid; and this mode of procedure in stages possesses the distinct advantage

that the final product is essentially homogeneous, whereas this is not the case when the sugar is oxidised direct with nitric acid (compare Hirst, J., 1926, 350). Only a trace of *d*-dimethoxysuccinic acid, which was isolated as the diamide, was found to be present in the oxidation product. The absence of any trace of tetramethoxymucic acid excludes the possibility of a 1 : 6-oxide linking. The *l*-arabotrimethoxyglutaramide was recognised by its rotation $[\alpha]_D$ + 50° in water, and by its decomposition on heating at 230°. Direct comparison with an authentic specimen prepared from arabinose (Hirst and Robertson, J., 1925, **127**, 358) indicated its identity. When the ester was treated with methylamine in methyl-alcoholic solution, the crystalline *l-arabotrimethoxyglutaromethylamide* (III) separated as needles, m. p. 173°; $[\alpha]_D^{18°}$ + 59·9°. Comparison with an authentic specimen prepared by an alternative method, *viz.*, from pure methyl *l*-arabotrimethoxyglutarate obtained from normal trimethyl arabinose, proved its identity (Haworth and Jones, this vol., p. 2349). Since the crystalline methylamide has a definite m. p. (without decomposition) the comparison could in this case be made by means of a mixed m.-p. determination, a procedure which cannot be followed with equal certainty with the crystalline amide.

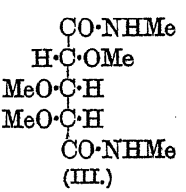
These results prove the constitution of the tetramethyl δ-galactonolactone, and lead by inference to the conclusion that crystalline tetramethyl galactose possesses an amylene-oxide structure, as was previously suggested on other grounds (Pryde, J., 1923, **123**, 1808; Haworth, Ruell, and Westgarth, *loc. cit.*). This sugar should now be definitely indexed as 2 : 3 : 4 : 6-tetramethyl galactose (I), and the derived lactone as 2 : 3 : 4 : 6-tetramethyl galactonolactone (II). By inference, it is concluded that free galactose possesses the amylene-oxide structure, since there appear to be no reasonable grounds for postulating a difference in ring structure between galactose and α- and β-methylgalactosides (compare Drew and Haworth, J., 1926, 2303).



(I.)



(II.)



(III.)

EXPERIMENTAL.

Preparation of Tetramethyl Galactose.—Octamethyl lactose (Haworth and Leitch, J., 1918, **113**, 198) was hydrolysed in the

usual manner with aqueous hydrochloric acid, the neutralised solution being thereafter extracted with chloroform to remove the tetramethyl galactose. The crude tetramethyl galactose so obtained was purified by conversion into the crystalline anilide (m. p. 192°), which is easily obtainable in a very pure state (Irvine and McNicoll, J., 1910, 97, 1454). Hydrolysis of the anilide with 5% aqueous hydrochloric acid (Haworth, Ruell, and Westgarth, J., 1924, 125, 2473), followed by distillation of the product, now gave a pure specimen of tetramethyl galactose in the form of a syrup containing both the α- and β-modifications of the sugar; $n_D^{13°}$ 1·4682; $[\alpha]_D^{15°}$ + 118° in water ($c = 1·9$; equilibrium value). A small quantity of this syrup dissolved in ether yielded crystals when rubbed with a glass rod during the evaporation of the solvent. When nucleated with this crystalline material, the main bulk crystallised readily to give in good yield solid tetramethyl galactose, m. p. 71—72° after recrystallisation from light petroleum (compare Schlubach and Moog, *loc. cit.*).

Preparation of Tetramethyl δ-Galactonolactone.—For comparative purposes three methods were employed for the preparation of this lactone. In the first, the directions given by Haworth, Ruell, and Westgarth were followed, the liquid tetramethyl galactose mentioned above being used; the resulting lactone was a liquid whose physical constants were in exact agreement with those previously recorded. The second method involved the preparation of the lactone from crystalline tetramethyl galactose, the experimental conditions being otherwise unchanged. The product (b. p. with bath temperature 163—166°/0·18 mm.; $n_D^{14°}$ 1·4606) was a liquid which could not be induced to crystallise (0·1603 G. required 6·9 c.c. of N/10-sodium hydroxide for neutralisation. Calc.: 6·85 c.c.).

A polarimetric study of its behaviour in aqueous solution showed $[\alpha]_D$ + 157° approx. (initial value by extrapolation); $[\alpha]_D$ + 26·2° (equilibrium value after 14 hours). The values of $[\alpha]_D$ plotted against time gave a curve indistinguishable from that already recorded by Haworth, Ruell, and Westgarth (*loc. cit.*) and by Drew, Goodyear, and Haworth (this vol., p. 1237). The third method for preparing the lactone in a highly pure condition lay in the regeneration of the compound from the crystalline phenylhydrazide of the corresponding 2:3:4:6-tetramethyl galactonic acid. The lactone (1·9 g.) prepared from the liquid tetramethyl galactose (α+β forms) was mixed with the theoretical amount of freshly distilled phenylhydrazine and sufficient ether to form a homogeneous solution. The mixture was heated on the water-bath for 30 minutes and a solid mass remained. This was broken up, rubbed with ether, and filtered, giving a white, crystalline solid (2·55 g.; m. p. 135—137°), which was the pure *phenylhydrazide*

of tetramethyl galactonic acid. Recrystallisation from ether or benzene failed to raise the m. p. (Found : C, 56·25; H, 7·5; N, 8·5; OMe, 32·4. $C_{16}H_{26}O_6N_2$ requires C, 56·1; H, 7·6; N, 8·2; OMe, 36·3%). The phenylhydrazide (1·9 g.) was treated with a slight excess of $N/10$-aqueous hydrochloric acid (60 c.c.) and heated at 100° for 3 hours. This gave a pale yellow solution, which was evaporated to dryness under diminished pressure, the residue being finally dried for 2 hours at 100°/12 mm. The lactone was then extracted by dry chloroform containing a little ether, and after removal of the solvent and thorough drying, it was finally purified by distillation to give a colourless liquid (1·09 g.), $n_D^{13°}$ 1·4609; $[\alpha]_D$ + 156° (initial value). Equilibrium value after 14 hours +26·1°. 0·3139 G. required for neutralisation 13·6 c.c. of $N/10$-sodium hydroxide (Calc. : 13·4 c.c.).

Oxidation of Tetramethyl δ-Galactonolactone with Nitric Acid.—The lactone used was a specially purified specimen ($n_D^{13°}$ 1·4606) which conformed exactly in its polarimetric behaviour to the standards accepted for the pure lactone. A solution containing 5 g. of lactone in 40 c.c. of nitric acid (d 1·42) was gently warmed for ½ hour at 50—60°, whereupon oxidation commenced. The reaction continued slowly and smoothly as the temperature was gradually raised to 90°, and appeared to be complete after 6 hours at this temperature. Throughout the subsequent dilution, removal of the nitric acid and water by distillation under diminished pressure, and esterification of the oxidation products with methyl alcohol, the usual methods were employed, details of which have already been published. The esterified product was obtained as a clear, mobile liquid weighing 4·33 g. This was neutral to litmus and without action on Fehling's solution. Distillation gave (I) 3·6 g., b. p. 95°/0·08 mm., $n_D^{15°}$ 1·4359, $[\alpha]_D^{20°}$ + 44·7° in water ($c = 1·2$); (II) 0·56 g., b. p. 110°/0·18 mm., $n_D^{15°}$ 1·4369, $[\alpha]_D^{20°}$ + 33·8° in water ($c = 2$). The first fraction agreed in physical properties with methyl *l*-arabotrimethoxyglutarate (Hirst and Robertson, *loc. cit.*) and analysis showed it to be very nearly pure (Found : C, 47·6; H, 7·3; OMe, 58·8. Calc. for $C_{10}H_{18}O_7$: C, 48·0; H, 7·2; OMe, 62·0%).

Confirmation was obtained by the formation of the corresponding amide. The ester (0·97 g.) dissolved in methyl-alcoholic ammonia (10 c.c.) gave after 15 hours a first crop of crystals in the form of needles, m. p. 270—278° (decomp.), which appeared to be a mixture of *d*-dimethoxyglutaramide and *l*-arabotrimethoxyglutaramide (Found : C, 41·6; H, 7·15; N, 14·0; OMe, 33·4%). The main crop, which crystallised in the course of a few days, weighed 0·55 g. (yield 63% of theory). Recrystallised from methyl alcohol, this material decomposed at 230° with evidence of melting beginning at 228°, and it was shown to be *l*-arabotrimethoxyglutaramide by com-

parison with an authentic specimen; $[\alpha]_D$ + 50·2° in water (c = 1·14) (Found: C, 43·2; H, 7·2; N, 12·4; OMe, 40·1. Calc.: C, 43·6; H, 7·3; N, 12·7; OMe, 42·2%).

The corresponding methylamide was prepared by dissolving the ester (0·46 g.) in methyl alcohol (6·0 c.c.) saturated with methylamine, and allowing the solution to remain at room temperature for 4 days. After removal of the solvent in a vacuum desiccator, the resulting solid mass was recrystallised from ethyl acetate, giving needles; m. p. 172°, alone or mixed with an authentic specimen of the methylamide (Haworth and Jones, *loc. cit.*) prepared from pure methyl *l*-arabotrimethoxyglutarate; yield 0·4 g.; $[\alpha]_D^{15°}$ + 59·9° (Found: C, 48·3; H, 8·2; N, 10·9; OMe, 35·55. Calc.: C, 48·35; H, 8·1; N, 11·2; OMe, 36·4%).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCCXXV.—1:3:4:6-*Tetramethyl* (γ-)*Fructose and* 2:3:5-*Trimethyl* (γ-)*Arabinose. Oxidation of* d- *and* l-*Trimethyl* γ-*Arabonolactone.*

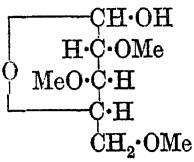
By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and ABRAHAM LEARNER.

THE representative of the so-called γ-sugars in the arabinose series was first prepared as *l*-trimethyl γ-arabinose by Baker and Haworth (J., 1925, **127**, 365), who assigned a butylene-oxide structure to this sugar for the reason that it gave on oxidation with bromine water a crystalline trimethyl arabonolactone which was characterised as a γ-lactone. The latter conclusion was confirmed by Haworth and Nicholson (J., 1926, 1899), who showed that unsubstituted γ-arabonolactone prepared by oxidation of *l*-arabinose gave, on methylation, the same crystalline trimethyl derivative as Baker and Haworth had isolated by oxidation of trimethyl γ-arabinose (I).

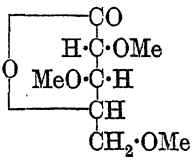
The allocation of a butylene-oxide structure to both the lactone and the sugar was supported by the comparison of the rate of hydrolysis of the former with that of other γ-lactones (Charlton, Haworth, and Peat, J., 1926, 89; Drew, Goodyear, and Haworth, this vol., p. 1242). These conclusions have now been tested by degradation of *l*-trimethyl γ-arabonolactone by oxidative methods which are herein described.

In the meantime, the corresponding optical enantiomorph, *viz.*, *d*-trimethyl γ-arabonolactone, has also been isolated (Avery, Haworth, and Hirst, this vol., p. 2308) from the products of oxi-

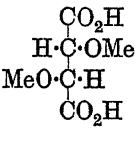
dation of tetramethyl γ-fructose. The crystalline form, melting point, and magnitude of specific rotation of the two specimens were identical, but the sign of rotation was opposite. It became evident that the final proof of the constitution of this lactone was an issue of considerable importance in the structural chemistry of the sugars, since the solution of the problem of the structure of sucrose rested upon this proof. Accordingly, the two enantiomorphous specimens of trimethyl γ-arabonolactone were submitted independently to oxidation with nitric acid (*d* 1·42). The product isolated from the *l*-trimethyl γ-arabonolactone (II) was recognised as *d*-dimethoxysuccinic acid (III), inasmuch as it gave a crystalline amide and a crystalline methylamide which were identical with authentic specimens specially prepared from *d*-tartaric acid.



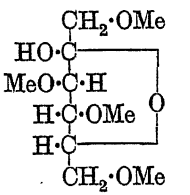
(I.)



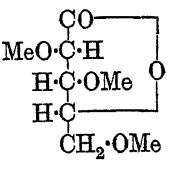
(II.)



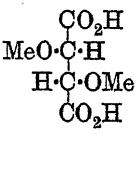
(III.)



(IV.)



(V.)



(VI.)

Similarly, the *d*-variety of trimethyl γ-arabonolactone (V), which had been isolated from tetramethyl γ-fructose (IV), gave on oxidation *l*-dimethoxysuccinic acid (VI); this was characterised as the crystalline amide and methylamide, which were identified as before by direct comparison with authentic specimens prepared for this purpose from *l*-tartaric acid (Haworth and Jones, this vol., p. 2349).

These experimental results must be considered in relation to the structurally isomeric trimethyl δ-arabonolactone, which has been shown to be amylene-oxidic and to give rise on oxidation (Haworth and Jones, *loc. cit.*) to *l*-arabotrimethoxyglutaric acid, which was similarly characterised through the crystalline methylamide (compare Hirst and Robertson, J., 1925, **127**, 358). It was therefore demonstrated that whilst normal trimethyl arabinose contains an amylene-oxide ring, the trimethyl γ-arabinose, on the other hand, has a butylene-oxide structure; that *l*-trimethyl γ-arabonolactone derived from the latter sugar must be indexed as 2 : 3 : 5-trimethyl arabonolactone, and that to the *d*-isomeride isolated in the manner

indicated above as a degradation product of the fructose residue in methylated sucrose is similarly to be assigned the constitution of *d*-2:3:5-trimethyl arabonolactone. These conclusions confirm in their entirety the inferences already drawn from the results of the earlier studies of the lactones and of the reference compounds herein described.

An additional point of interest which emerges from the further study of these lactones is that the two γ-lactones displayed great stability towards nitric acid, contrasting remarkably with the labile character of the corresponding δ-lactone of this series and also with other δ-lactones which have hitherto been submitted to oxidative degradation. This behaviour is in harmony with the distinctive properties of γ- and δ-lactones which have already been elucidated in the course of earlier work (Drew, Goodyear, and Haworth, *loc. cit.*).

EXPERIMENTAL.

Oxidation of l-*Trimethyl* γ-*Arabonolactone.*—Arabonic acid, obtained in the usual way from arabinose by the action of bromine water, was purified by conversion into the cadmium salt, which could be readily recrystallised from water in place of alcohol as mentioned in the literature. After removal of the cadmium as sulphide, the lactone was obtained on concentrating the aqueous solution (Bauer, *J. pr. Chem.*, 1884, **30**, 367; 1886, **34**, 46). *l*-Trimethyl γ-arabonolactone was then obtained by methylating arabonolactone (Haworth and Nicholson, *loc. cit.*). It had m. p. 30—32° alone or mixed with specimens prepared from arabonolactone and from trimethyl γ-arabinose (Baker and Haworth, *loc. cit.*); $[\alpha]_D$ −44° in water (initial value) decreasing to −25° after 20 days. A solution containing 1·7 g. of this material in 17 c.c. of nitric acid (*d* 1·32) was heated on the water-bath until reaction commenced at 95°. At this temperature, evolution of nitrous fumes took place slowly, and the oxidation was allowed to proceed for 7 hours at 95—100°. Even then no definite end-point had been reached, but the rate of reaction had become extremely slow. 35 C.c. of distilled water were then added, and the nitric acid was removed by distillation under diminished pressure with frequent additions of water. The product was thus obtained as a colourless syrup, which was esterified by digestion for 8 hours with 40 c.c. of methyl alcohol containing 1·6 g. of hydrogen chloride. The mineral acid was neutralised in the usual way with silver carbonate, the solvent evaporated, and the esterified oxidation product purified by distillation, which proceeded smoothly only after a preliminary heating for 3 hours at 120°. This effected the transformation of some methyl trimethylarabonate into the lactone of the corresponding acid. During the preliminary heating,

a small quantity of methyl oxalate was collected. The main fraction (A) distilled from a bath at 159—170°/16 mm., giving a colourless syrup (0·8 g.), n_D^{16} 1·4391; $[\alpha]_D^{16°}$ +41·5° in water (c = 1·1; initial value) (0·1041 G. required, as lactone, 2·0 c.c. of N/10-sodium hydroxide for neutralisation; for hydrolysis and neutralisation, 8·7 c.c.). These properties correspond with those required by a mixture containing approximately 65% of methyl *d*-dimethoxysuccinate and 35% of *l*-trimethyl arabonolactone. The presence of methyl *d*-dimethoxysuccinate was proved by the formation of the corresponding amide and methylamide. The distillate (A) (0·23 g.), dissolved in 2·3 c.c. of methyl-alcoholic ammonia, gave, after 40 hours, 0·07 g. of *d*-dimethoxysuccinamide, the identity of which was confirmed by comparison with an authentic specimen, melting to a dark liquid at 269°, decomposing rapidly at 283°; $[\alpha]_D$ +97° in water (c = 0·433) (Found: C, 40·7; H, 6·8; OMe, 33·7. Calc. for $C_6H_{12}O_4N_2$: C, 40·9; H, 6·8; OMe, 35·2%). Again, 0·13 g. of the distillate (A), dissolved in 1·3 c.c. of methyl alcohol saturated with methylamine, gave crystals on evaporation of the solvent after 3 days. These recrystallised from ethyl acetate as long needles (yield, 0·06 g.), m. p. 205—206°, alone or mixed with an authentic specimen of the methylamide of dimethoxysuccinic acid prepared from *d*-tartaric acid (Haworth and Jones, *loc. cit.*). No trace of the amide or methylamide of trimethoxyglutaric acid could be detected in the course of these experiments.

Oxidation of d-*Trimethyl γ-Arabonolactone.*—The *d*-trimethyl γ-arabonolactone was prepared from tetramethyl γ-fructose by the method described by Avery, Haworth, and Hirst (this vol., p. 2317); it had m. p. 33°; $[\alpha]_D$ +44·5° (initial value) in water ⟶ +25·5° (after 20 days). This material (2·5 g.) was dissolved in 28 c.c. of nitric acid (*d* 1·42), the procedure thereafter being similar to that described above. A small quantity of oxalic acid (identified as methyl oxalate) was formed during the oxidation. The esterified product was distilled from a bath at 155—160°/13 mm., and gave 1·42 g. of colourless syrup (B), $n_D^{15°}$ 1·4400; $[\alpha]_D$ − 50° in methyl alcohol (c = 1·50) (0·0581 G. required 1·0 c.c. of N/10-sodium hydroxide for neutralisation, as lactone, and 4·9 c.c. of N/10-sodium hydroxide for complete hydrolysis and neutralisation). These figures correspond to a mixture containing 32% of methyl *l*-dimethoxysuccinate and 68% of *d*-trimethyl γ-arabonolactone. The amide [yield 0·202 g. from 0·50 g. of the product (B)], prepared in the usual way, was obtained as long needles, which melted after preliminary darkening at 245—250° to a dark liquid at 270° (rapid decomp. at 283°); $[\alpha]_D^{18°}$ − 94° in water (c = 0·9) (Found: C, 40·9; H, 6·8; N, 15·7; OMe, 33·2. Calc. for $C_6H_{12}O_4N_2$: C, 40·9; H,

6·8; N, 15·9; OMe, 35·2%). The corresponding methylamide was also prepared as long needles (from ethyl acetate), m. p. 204—205° alone or mixed with a specimen of the methylamide of *l*-dimethoxysuccinic acid prepared from *l*-tartaric acid (Haworth and Jones, *loc. cit.*).

No trace of the amide or methylamide of trimethoxyglutaric acid was found in the mother-liquors arising from these experiments.

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UNIVERSITY OF BIRMINGHAM,
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CCCXXVI.—*The Structure of the Normal and γ-Forms of Tetramethyl Glucose. Oxidation of Tetramethyl δ- and γ-Gluconolactones.*

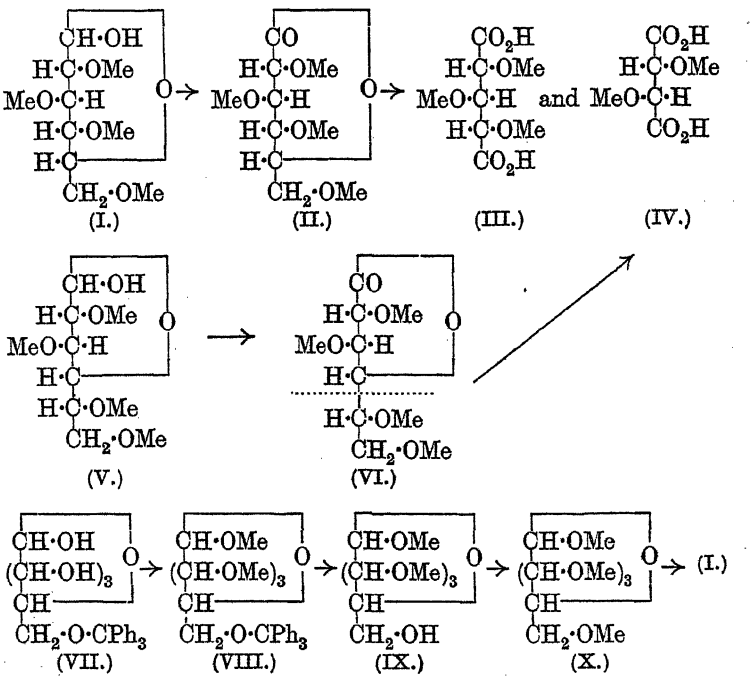
By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and ERNEST JOHN MILLER.

IN a paper on the revision of the structural formula of glucose (Charlton, Haworth, and Peat, J., 1926, 89), the constitution assigned to the usual form of tetramethyl glucose represented this sugar as an amylene oxide, whilst the butylene-oxide formula was assigned to its labile or γ-form. The experimental basis for these conclusions was the recognition that the lactones derived from these two sugars were, respectively, δ- and γ-lactones. These conclusions have been tested in the course of subsequent work (Drew, Goodyear, and Haworth, this vol., p. 1237), and further experimental data are now furnished which confirm the recognition of the two forms of the methylated sugar as 2 : 3 : 4 : 6-tetramethyl glucose (*i.e.*, the normal crystalline variety) and 2 : 3 : 5 : 6-tetramethyl glucose (the labile or γ-variety, which is a liquid). This inference with respect to the normal form of the sugar was supported by the direct oxidation of the normal crystalline sugar with nitric acid (Hirst, J., 1926, 350).

Tetramethyl δ-gluconolactone has been prepared in a condition of greater purity by preliminary conversion into the crystalline phenylhydrazide (m. p. 115°; $[\alpha]_D + 42{\cdot}1°$ in ethyl alcohol) of the corresponding acid, followed by regeneration of the lactone from this derivative. The physical constants of the regenerated lactone differ but slightly from those already recorded, and the substance is still recognised as a liquid. On the other hand, the lactone derived

by oxidation of the liquid tetramethyl γ-glucose is crystalline, and the physical constants are also on record (Drew, Goodyear, and Haworth, *loc. cit.*).

The study of these two lactones has now been continued by the application of the method of direct oxidation with nitric acid. Tetramethyl δ-gluconolactone, when treated with this reagent, gave a mixture of methoxyglutaric and methoxysuccinic acids, which were separated and identified through their crystalline amides and methylamides. Whilst the comparison of the amides with authentic specimens could be made with a considerable measure of certainty, yet, for reasons already explained (Haworth and Jones, this vol., p. 2349), it appeared to be advantageous to strengthen the validity of such comparisons by the adoption of the methylamides as reference compounds; but it should be added that the preparation of the amides enables a more satisfactory estimate to be made of the yields of the products of oxidation. The experiments have shown that the δ-lactone is



degraded to give a considerable yield (47%) of *i*-xylotrimethoxyglutaric acid (III) and a smaller yield (20%) of *d*-dimethoxysuccinic acid (IV), since the methylamides of these products were shown to be identical with authentic specimens prepared from other

sources. The isolation of the xylotrimethoxyglutaric acid affords definite proof that the oxygen of the oxide ring cannot be attached to carbon atom 2, 3, or 4, since the stereochemical arrangement of the groups associated with these carbon atoms is preserved in the *i*-xylotrimethoxyglutaric acid. On the other hand, the possibility of the attachment of the oxygen of the ring to carbon atom 6 in normal glucose derivatives is excluded by a large number of observations, amongst which may be mentioned (1) the oxidation of methylglucoside to the methylglucoside of glycuronic acid (Smolenski, *Rocz. Chem.*, 1923, **3**, 153); (2) the preparation herein described of 2 : 3 : 4-trimethyl β-methylglucoside (IX) [which is readily converted into normal tetramethyl methylglucoside (X)] from 6-triphenylmethyl glucose (VII), the constitution of which has been proved by Helferich, Klein, and Schäfer (*Annalen*, 1926, **447**, 19). The only remaining point for the attachment of the oxygen of the ring is the 5-position. The conclusion is therefore drawn that the structural formula (II) represents the constitution of tetramethyl δ-gluconolactone, and thus the formula (I), which represents crystalline tetramethyl glucose as an amylene oxide, is confirmed.

Similar experiments were conducted on the degradative oxidation of tetramethyl γ-gluconolactone, and these revealed the greater stability of this lactone towards nitric acid as compared with the δ-lactone. A further distinction is that a portion of the lactone appeared to undergo very profound degradation during the oxidation, a circumstance which has a definite bearing on the constitution of the substance. The only dibasic acids definitely recognised in the products from this treatment were oxalic acid and *d*-dimethoxysuccinic acid (IV), which was isolated as the amide and methylamide, both of which are crystalline, the latter compound being compared with an authentic specimen of the methylamide obtained ultimately from *d*-tartaric acid (compare Haworth and Jones, *loc. cit.*). An exhaustive but unsuccessful search was made for the presence of a glutaric acid derivative, the experimental conditions being such that the presence of a derivative of this acid could easily have been detected had it been formed. The isolation of *d*-dimethoxysuccinic acid from tetramethyl γ-gluconolactone proves definitely that the oxygen of the oxide ring cannot be attached to carbon atom 2 or 3, and thus the propylene-oxide formula for γ-glucose derivatives, advocated by Irvine and Patterson (J., 1922, **121**, 2152), is definitely disproved. Again, the oxygen of the ring cannot be attached at position 6, since tetramethyl γ-gluconolactone is derivable (in two stages) from 2 : 3 : 6-trimethyl glucose (Charlton, Haworth, and Peat, *loc. cit.*) but not from the 2 : 3 : 4-isomeride. The failure to isolate trimethoxyglutaric acid, when considered in relation to the

fact that the amylene-oxide structure has already been assigned to the δ-lactone, suffices to exclude the possibility of attachment of the oxide ring at carbon atom 5, and it follows, therefore, that the oxygen of the ring must be linked to carbon atom 4. Tetramethyl γ-glucose and its related lactone are thus seen to have a butylene- or γ-oxide structure (V and VI).

In the above reaction, scission of the lactone had occurred at the point indicated by the dotted line drawn between the fourth carbon atom, which is attached to one junction of the oxide ring, and the fifth carbon atom of the chain. Consideration of alternative methods by which a compound of formula (VI) could undergo scission appears to supply a reason for the failure to obtain *d*-dimethoxysuccinic acid in a yield greater than 20%. A comparison with the course which the oxidation of the δ-lactone takes, giving both a glutaric and a succinic acid derivative, suggests that if an analogous breakdown of the γ-lactone occurred, this might lead to the formation, not only of *d*-dimethoxysuccinic acid, but also of methoxymalonic acid. The isolation of the latter, which we failed to recognise, would be rendered difficult by reason of its instability. Indications were given of the presence of a dimethyl saccharolactone, which had presumably been formed by the oxidation of the terminal $-CH_2OMe$ group at position 6 to a carboxyl group. A similar oxidation of this terminal group is recorded in the case of 2 : 3 : 6-trimethyl glucose (Irvine and Hirst, J., 1922, **121**, 1213) and also with 2 : 3 : 5-trimethyl arabinose (Baker and Haworth, J., 1925, **127**, 365).

Incidentally, it may be remarked that the butylene-oxide ring structure of the γ-glucose residue in glucose-diacetone receives confirmation. Support is thus given to the inferences drawn by Karrer and Hurwitz (*Helv. Chim. Acta*, 1921, **4**, 728), although their conclusions and experimental methods were severely attacked by Irvine and Patterson (J., 1922, **121**, 2155), whose criticisms are seen to have been based on a misapprehension as to the structure of the monomethyl derivative of glucose-diacetone.

EXPERIMENTAL.

Preparation of Tetramethyl δ-Gluconolactone (II).—Specially purified tetramethyl glucose (I) (m. p. 86°) was converted into tetramethyl gluconic acid by digestion with bromine water at 60° until the solution no longer gave a positive Fehling's test. The lactone was then isolated by the usual method as a colourless liquid, b. p. 106—107°/0·04 mm.; $n_D^{14°}$ 1·4566; $[\alpha]_D^{22°}$ + 99° in water ($c = 2·27$; initial value), decreasing rapidly to the constant value $[\alpha]_D^{22°}$ + 30·8° after 8 hours. Attempts to induce the lactone to crystallise were unsuccessful, and further purification was effected

by regenerating the compound from the crystalline phenylhydrazide of the corresponding tetramethyl gluconic acid. The phenylhydrazide was prepared by the method described by Charlton, Haworth, and Peat (*loc. cit.*); recrystallised from benzene, it had m. p. 115°, $[\alpha]_D$ + 42·1° in ethyl alcohol (c = 1·0). Treatment with 5% aqueous hydrochloric acid for 3 hours on the water-bath served to regenerate the acid, and the lactone was isolated by evaporating the solution to dryness under diminished pressure and extracting the residue with dry chloroform admixed with a little ether. The phenylhydrazine hydrochloride was filtered off, the solvent evaporated under diminished pressure, and the residual syrup purified by repeated distillation in a high vacuum. The final distillate had b. p. 101°/0·06 mm.; $n_D^{14°}$ 1·4565; $[\alpha]_D^{18°}$ + 101° in water (c = 2·06; initial value), decreasing in the course of 8 hours to a constant value $[\alpha]_D^{18°}$ 29·6°. The regenerated lactone was therefore almost identical in physical properties with the original specimen, and further repeated attempts to induce crystallisation were unsuccessful.

Oxidation of Tetramethyl δ-Gluconolactone.—A specimen of the lactone (4·0 g.), which had been purified as above, was dissolved in nitric acid (32 c.c.; d 1·42). A vigorous reaction took place at 70°. This was moderated by cooling the reaction vessel, and after 1 hour the temperature was raised to 90° and the reaction allowed to proceed to completion (6 hours). The solution was diluted with water and the reaction product isolated as the methyl ester as described below for the tetramethyl γ-gluconolactone. The esterified product was distilled, giving a colourless liquid (A) (yield, 2·7 g.), b. p. 98—100°/0·05 mm.; $n_D^{15°}$ 1·4400; $[\alpha]_D^{16°}$ + 21·7° in water (c = 2·2). This material appeared to be a mixture containing approximately 30% of methyl *d*-dimethoxysuccinate and 70% of methyl *i*-xylotrimethoxyglutarate (Found: C, 46·8; H, 7·2; OMe, 61·3. Calc.: C, 47·6; H, 7·1; OMe, 61·5%). The presence of both these substances was proved by the isolation of the corresponding crystalline amides and methylamides.

Amides.—The distillate (A) (1·0 g.) was dissolved in 6 c.c. of methyl alcohol saturated with ammonia and kept for 70 hours, during which 0·19 g. of *d*-dimethoxysuccinamide separated as clusters of long needles. These darkened when heated above 200°, melted at 270° to a dark liquid, and decomposed rapidly at 283°; $[\alpha]_D$ + 94° in water (c = 0·51). Direct comparison with an authentic specimen established the identity of this material. The disturbance of the solution consequent upon the removal of the dimethoxysuccinamide induced rapid crystallisation of a second substance of markedly different habit and appearance; this was filtered off after 4 days, and washed with methyl alcohol and ether; yield, 0·25 g.;

m. p. 197°. It was optically inactive. Comparison with an authentic specimen prepared from xylose proved its identity with *i*-xylotrimethoxyglutaramide.

Methylamides.—The distillate (A) (1·4 g.) was dissolved in methyl alcohol (8 c.c.) saturated with methylamine; after 3 days, the solvent and the excess of methylamine were removed by evaporation in a vacuum desiccator. The residual solid mass was dissolved in 30 c.c. of boiling ethyl acetate, the solution cooled, and the resulting crystals were washed with a little ethyl acetate and then with ether; m. p. 158—163° (yield, 0·34 g.). Recrystallisation from ethyl acetate now gave the methylamide of *i*-xylotrimethoxyglutaric acid in long needles which, alone or when mixed with an authentic specimen prepared from xylose, melted at 165—167°. The substance was optically inactive (Found: C, 48·3; H, 8·3; N, 11·5; OMe, 34·3. Calc. for $C_{10}H_{20}O_5N_2$: C, 48·4; H, 8·1; N, 11·3; OMe, 37·5%). The mother-liquor from the first crop of crystals, on evaporation to dryness under diminished pressure, gave a residue which was recrystallised three times from ether–ethyl acetate (equal vols.); yield, 0·05 g.; long needles, m. p. 206°, alone or when mixed with a specimen of the methylamide of *d*-dimethoxysuccinic acid prepared from *d*-tartaric acid.

Oxidation of Tetramethyl γ-Gluconolactone (VI).—The lactone used was a crystalline specimen, m. p. 26—27°, conforming exactly with the polarimetric standards for the material prepared by Drew, Goodyear, and Haworth from tetramethyl γ-glucose (this vol., p. 1242). This lactone (3·4 g.) was dissolved in nitric acid (26 c.c.; *d* 1·42) and heated on the water-bath at 80° for ½ hour, but showed no appreciable change; the temperature was accordingly raised to 90°, but the reaction was sluggish and had not reached completion after 5 hours at this temperature; nevertheless it was decided to examine the products at this stage. The solution was diluted with water and the nitric acid removed by distillation under diminished pressure with frequent additions of water. The residue was esterified with methyl alcohol (50 c.c.) containing hydrogen chloride (2·4 g.), the mineral acid neutralised with silver carbonate, and the filtered solution evaporated to a syrup which contained a small quantity of mineral matter. The latter was removed by dissolving the syrup in benzene, and the subsequent evaporation of the solvent served to remove all traces of water. Distillation of the esterified product was difficult owing to the presence in small amount of a substance which underwent transformation when heated at 120° in a vacuum. This gave a minute quantity of a volatile liquid, probably methyl alcohol, of which the sudden evolution in the form of vapour caused violent bumping. The reaction product was there-

fore heated at 135—140°/11 mm. until this transformation was complete. Distillation now proceeded smoothly and gave (*a*) 0·3 g. of a colourless liquid which solidified in the receiver and was mainly methyl oxalate—some of this material had been collected during the preliminary heating; (*b*) 0·7 g., b. p. 135—140°/12 mm., $n_D^{15°}$ 1·4365; (*c*) 0·85 g., b. p. 140—160°/12 mm., $n_D^{15°}$ 1·4442, $[\alpha]_D$ + 57° in water ($c = 1·1$; initial value), decreasing to + 50° after several days; (*d*) residue, 0·2 g. Fractions (*b*) and (*c*) were colourless liquids which developed an acid reaction in aqueous solution; neutralisation of these solutions indicated the presence of a lactone. This observation, together with previous experience gained in distilling the esters of γ-hydroxy-acids, suggested that the transformations which preceded distillation were due to the elimination of methyl alcohol from the ester of a γ-hydroxy-acid, with the formation of a lactone. The presence of a lactone was further demonstrated by the change in rotation of the aqueous solution when kept for several days.

Amides and Methylamides.—Both fractions (*b*) and (*c*) yielded crystalline *d*-dimethoxysuccinamide when dissolved in methyl-alcoholic ammonia. In one experiment, 0·120 g. of (*b*) gave after 4 days 0·064 g. of long needles, which were filtered off and washed with methyl alcohol and ether; these darkened at 245°, began to melt with decomposition at 270°, and decomposed entirely at 283°. Control experiments made in the same apparatus and under identical conditions, in which specimens of the *d*-dimethoxysuccinamide prepared from *d*-tartaric acid were employed, gave identical results; $[\alpha]_D^{20°}$ + 95° ($c = 1·1$) (Found: C, 40·8; H, 7·1; N, 15·7; OMe, 34·7. Calc. for $C_6H_{12}O_4N_2$: C, 40·9; H, 6·8; N, 15·9; OMe, 35·2%). Further proof of identity was furnished by preparing the corresponding methylamide. From 0·15 g. of fraction (*b*) in 1·1 c.c. of methyl alcohol saturated with methylamine, a mixture of syrup and crystals was obtained by removal of the solvent under diminished pressure. The crude crystalline material weighed 0·06 g., and on recrystallisation from ethyl acetate gave needles which, alone or mixed with an authentic specimen of the methylamide of *d*-dimethoxysuccinic acid prepared from *d*-tartaric acid, melted at 204° (Found: C, 46·7; H, 7·9; N, 13·8. Calc. for $C_8H_{16}O_4N_2$: C, 47·05; H, 7·8; N, 13·7%).

Fraction (*c*) (0·500 g.) gave analytically pure *d*-dimethoxysuccinamide (0·068 g.), m. p. 270° (decomp. 282°) (Found: C, 40·9; H, 7·1; N, 15·5%). An exhaustive examination was made of the syrup remaining after evaporation of the mother-liquors from the amide formations. A further very minute quantity of *d*-dimethoxysuccinamide was obtained, but no other crystalline material. In particular, no trimethoxyglutaramide could be isolated. For this

examination the whole of the remaining portions of (*b*) and (*c*) were treated with methyl alcohol and ammonia. *Titration of fraction* (*c*): 0·1040 G. required 3·9 c.c. of *N*/10-sodium hydroxide for neutralisation of the lactone portion, and 8·3 c.c. (total) of *N*/10-sodium hydroxide for hydrolysis and neutralisation. These figures, in conjunction with the yield of crystalline amide (which gives an approximate estimate of the amount of dimethoxysuccinic ester present), indicated that the major portion of (*c*) consisted of a dibasic lactone-ester, possibly the methyl ester of dimethyl saccharolactone. The amount of unchanged tetramethyl γ-gluconolactone was apparently very small, and this was confirmed by the failure to isolate the characteristic and easily recognisable crystalline phenylhydrazide of the corresponding tetramethyl gluconic acid.

[With ABRAHAM LEARNER.]

Methylation of Triphenylmethyl Glucose (VII).—Crystalline triphenylmethyl glucose (3·0 g.) (as prepared by Helferich, Klein, and Schäfer, *loc. cit.*) was dissolved in methyl iodide and treated in the usual manner with silver oxide. The operation was repeated three times, and the crude product so obtained gave OMe, 21·7 (Calc. for $C_{29}H_{34}O_6$: OMe, 25·9%), the low value being attributable to the presence of a small quantity of triphenylcarbinol. The methylated product was hydrolysed by 100 c.c. of methyl alcohol containing 0·5% of hydrogen chloride. After being kept for 5 minutes at 65° and for 2½ hours at room temperature, the solution was neutralised with silver carbonate. The residual syrup obtained after evaporation of the solvent was extracted with warm water. The aqueous extract, evaporated at 50° under diminished pressure, yielded a syrup which crystallised partially when nucleated with a specimen of 2 : 3 : 4-trimethyl β-methylglucoside. Purification of this material by distillation from a bath at 135°/0·1 mm. yielded a colourless liquid which crystallised on cooling. The crystals were drained on porous earthenware, and recrystallised from light petroleum, giving matted needles; these, alone or when mixed with a specimen of 2 : 3 : 4-trimethyl β-methylglucoside (IX) prepared from gentiobiose, melted at 92—93° (Found: C, 50·7; H, 8·6. Calc. for $C_{10}H_{20}O_6$: C, 50·8; H, 8·5%).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCCXXVII.—*Acid and Salt Effects in Catalysed Reactions. Part XI. The Hydrolysis of Ethyl Acetate and the Catalytic Catenary.*

By HARRY MEDFORTH DAWSON and WILLIAM LOWSON.

THE detailed study of the velocity of the acetone–iodine reaction in the presence of weak acids and the corresponding salts (see previous papers) has shown that catalytic effects of considerable magnitude are to be attributed to the undissociated acid and also to the acid anion. For various other reactions, evidence in favour of the catalytic activity of the undissociated acid has already been furnished by observations on the changes in reaction velocity which occur when the concentration of the acid is altered or when the corresponding salt is added, and an attempt has been made to explain the facts in terms of the so-called dual theory. According to later developments, the dual theory would seem to represent a very incomplete statement of the actual relations, and in the expectation that other reactions would show catalytic effects parallel with those observed in the action of iodine on acetone, measurements have been made of the rate of hydrolysis of ethyl acetate in presence of mixtures of acetic acid and sodium acetate. The mixtures used are represented by the general formula cHA + xMA, in which c is constant and x is variable.

Preliminary observations with 0·1N-acid solutions showed that, with a continually increasing salt content, the velocity falls at first to a minimum, and increases later in such a way that it can be represented as a linear function of x. Since for such a series of acid–salt mixtures the concentration of the hydroxyl ion is proportional to x, it was thought possible that the effects could be accounted for by the joint action of the hydrogen and hydroxyl ions. The reaction velocities calculated on this hypothesis are, however, much smaller than those observed, as may be illustrated by reference to the data for the most concentrated salt solution ($x = 2{\cdot}5$), for which the observed velocity is about 8 times as great as the calculated value. Furthermore, when the observed velocity was plotted against the p_{H} value of the solutions, it was found that the minimum velocity corresponds approximately with $p_{\text{H}} = 5{\cdot}1$. This represents a hydrogen-ion concentration which is much larger than would be expected on the assumption that the hydrogen and hydroxyl ions are the only active catalytic agents. The isocatalytic point on the $\overset{+}{\text{H}}$–$\overset{-}{\text{OH}}$ catenary is actually given by $[\overset{+}{\text{H}}]_i = \sqrt{k_{\text{OH}}K_w/k_h}$ and by substituting $k_{\text{OH}}/k_h = 1000$ and $K_w = 10^{-14}$, this equation yields a hydrogen-ion concentration which corresponds with $p_{\text{H}} = 5{\cdot}5$.

It thus appears that the observed minimum-velocity (*M.V.*) point differs in respect of both velocity and hydrogen-ion concentration from the isocatalytic point characteristic of the $\overset{+}{H}$–$\overset{-}{O}H$ catenary, and this divergence led us to infer that the observed catalytic effects are connected with the catalytic activity of the undissociated acetic acid molecule and of the acetate anion. At the same time, the difference of 0·4 between the p_H values of the observed *M.V.* point and of the isocatalytic point on the $\overset{+}{H}$–$\overset{-}{O}H$ catenary is small enough to suggest that the anionic catalytic effect will not be confined to the acetate ion, but will be shared by the acetate and hydroxyl ions. The relations involved in such circumstances have been already considered in connexion with the catalytic effects exhibited by acetate buffers (compare this vol., p. 1146).

In accordance with the above views, it follows that the initial value of the specific reaction velocity (velocity referred to unit concentration of ester) in the presence of catalysts of the series $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$ should be represented by the formula

$$\begin{aligned} v &= v_h + v_a + v_{OH} + v_m \\ &= k_h[\overset{+}{H}] + k_a[\overset{-}{A}] + k_{OH}[\overset{-}{O}H] + k_m[HA] \quad . \quad . \quad (1) \end{aligned}$$

This equation may be reduced to the form $v = f[\overset{+}{H}]$, but for the present purpose it will be applied directly to the experimental observations.

Attention may, in the first instance, be directed to the results for those solutions which contain relatively large proportions of salt. In such solutions, the catalytic effect of the hydrogen ion can be almost neglected, whilst the concentration, and therefore the catalytic effect, of the undissociated acetic acid is constant. The observed changes in reaction velocity are therefore attributable to variations in the magnitude of the catalytic effects which are represented by the second and third terms in equation (1). If the straight line which expresses the connexion between v and x is extrapolated to $x = 0$, it is obvious that the intercept on the ordinate affords a measure of $v_m = k_m[HA] = 0{\cdot}1k_m$. The value thus obtained for k_m is $14{\cdot}5 \times 10^{-7}$.

Having thus determined k_m, the value of k_a may be derived from the observed velocity for any acid–salt mixture which falls on the linear portion of the v–x curve, in that k_a is the only remaining unknown quantity in equation (1). Rewriting this, we have

$$v_a = k_a x = v - k_h[\overset{+}{H}] - k_{OH}[\overset{-}{O}H] - k_m c_2$$

and from the data for the mixture $0{\cdot}1CH_3{\cdot}CO_2H + 2{\cdot}0CH_3{\cdot}CO_2Na$, the value obtained for k_a is $2{\cdot}0 \times 10^{-7}$.

The four coefficients being known, it is now possible to apply equation (1) to the interpretation of the experimental results.

EXPERIMENTAL.

The observations, which were made at 25° with an ester concentration of 0·4 mol. per litre,* are concerned solely with the initial velocity of hydrolysis. The molar concentration of acetic acid (y) produced during a measured time interval (t) was determined by titration of 25 c.c. samples of the solution with 0·1N-sodium hydroxide. The value of y is based on an increase of 1—2 c.c. in the volume of standard alkali required to neutralise the test sample, and it is estimated that the error involved is not greater than $\pm$ 0·03 c.c. The ester hydrolysed during the period of observation thus corresponds with 1—2% of the total ester present, and in the region of the minimal velocities the time required for this is about 2 months. The specific velocity is given by $v = y/at$, where a is the initial ester concentration, and this velocity, it may be noted, is identical with the initial value of k in the equation $k = 1/t \,.\, \log_e a/(a - y)$ for a unimolecular reaction, in that this equation reduces to the form $k = y/at$ when y is small compared with a.

The results of the experiments are summarised in Table I. Col. 1 shows the molar concentration (x) of acetate, col. 2 the hydrogen-ion concentration calculated from $[\overset{+}{H}] = K(c - [\overset{+}{H}])/(x + [\overset{+}{H}])$, and from this the values of $[\bar{A}]$, $[\bar{OH}]$, and [HA] are derived. Cols. 3—6 give the values of v_h, v_a, v_{OH}, and v_m, respectively, col. 7 the total calculated velocity $v = v_h + v_a + v_{OH} + v_m$, and col. 8 the corresponding observed specific velocity. The values employed for the various velocity coefficients are: $k_h = 6{\cdot}1 + 10^{-3}$,† $k_a = 2{\cdot}0 \times 10^{-7}$, $k_{OH} = 6{\cdot}5$, and $k_m = 14{\cdot}5 \times 10^{-7}$; for the ionisation constant of acetic acid $K = 1{\cdot}85 \times 10^{-5}$, and for the ionic product of water $K_w = 10^{-14}$.

With reference to Table I it may be noted that the catalytic effects produced by the acetate and hydroxyl ions are in a constant ratio, the value of which is given by $v_a/v_{OH} = k_aKc/k_{OH}K_w = 5{\cdot}7$. The general agreement between the numbers in the last two columns affords substantial evidence that the observed catalytic effects are

* On account of "salting-out," this was reduced to 0·2 mol./litre in the case of the three most concentrated salt solutions.

† This value is based on the results obtained in the detailed investigation of the hydrolysis of ethyl acetate under the catalytic influence of acetic acid (compare Dawson and Lowson, this vol., p. 2107).

TABLE I.

Hydrolysis of ethyl acetate at 25°. Catalyst: $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$.

						$v \cdot 10^7$.	
x.	$[\overset{+}{H}] \cdot 10^5$.	$v_h \cdot 10^7$.	$v_a \cdot 10^7$.	$v_{OH} \cdot 10^7$.	$v_m \cdot 10^7$.	Calc.	Obs.
0	135	82·3	—	—	1·43	83·7	81·6
0·005	34·5	21·0	0·01	—	1·45	22·5	23·0
0·015	12·2	7·45	0·03	—	1·45	8·9	9·1
0·03	6·15	3·75	0·06	0·01	1·45	5·3	5·2
0·05	3·7	2·25	0·10	0·02	1·45	3·8	4·2
0·07	2·65	1·62	0·14	0·03	1·45	3·25	3·3
0·10	1·85	1·13	0·20	0·04	1·45	2·8	2·5
0·20	0·92	0·56	0·40	0·07	1·45	2·5	2·5
0·35	0·53	0·32	0·70	0·12	1·45	2·6	2·45
0·50	0·37	0·22	1·00	0·17	1·45	2·85	3·0
1·0	0·185	0·11	2·00	0·35	1·45	3·9	3·7
1·5	0·123	0·07	3·00	0·52	1·45	5·05	5·5
2·0	0·092	0·05	4·00	0·70	1·45	6·2	6·2
2·5	0·074	0·04	5·00	0·88	1·45	7·4	7·6

due to the combined action of the hydrogen, acetate, and hydroxyl ions and of the undissociated acetic acid molecule.

In accordance with relations derived previously (Dawson and Dean, J., 1926, 2872; Dawson, this vol., p. 1146), the plot of the reaction velocity against p_H yields a symmetrical curve of catenary type. This curve is characterised by a minimum (isocatalytic) point, the hydrogen-ion concentration of which is given by

$$[\overset{+}{H}]_i = \sqrt{(k_a K c + k_{OH} K_w)/k_h}$$

and the corresponding minimum reaction velocity by

$$v_i = 2\sqrt{k_h(k_a K c + k_{OH} K_w)} + k_m c,$$

if k_m be neglected in comparison with k_h.

By substitution of the values for the various constants, these equations give $[\overset{+}{H}]_i = 8{\cdot}4 \times 10^{-6}$, or $(p_H)_i = 5{\cdot}07$, and $v_i = 2{\cdot}48 \times 10^{-7}$.

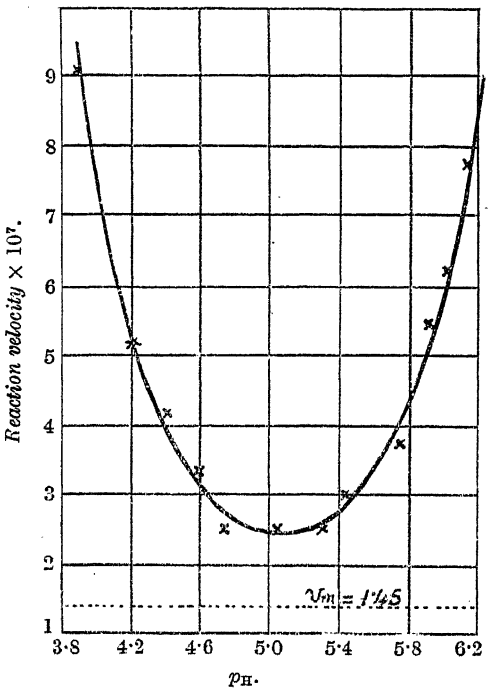
The diagram shows a catenary curve which has been drawn to show the connexion between the observed reaction velocities and the p_H values of the solutions. These p_H values are those derived on the assumption that the mass law is applicable to the ionisation of acetic acid and that the acetate is completely ionised. The co-ordinates of the apex of this catenary are obviously in close agreement with the above values of v_i and $(p_H)_i$.

The dotted horizontal line represents the velocity v_m due to the undissociated acetic acid. This may be regarded as the base line for the u—p_H curve, where u is the ionic reaction velocity.

According to the procedure adopted on p. 2445 for the evaluation of the coefficients k_m and k_a, the former was derived by extrapolation

of the linear portion of the v–x curve, whilst the latter was obtained from the slope of this line. Since the slope is determined by the joint action of the acetate and hydroxyl ions, a knowledge of k_{OH} is implied, and when the value of this coefficient is not known, other methods must be used for the derivation of k_a. These need not be described in the present paper, but reference may appropriately be made to an alternative method for the determination of k_m.

FIG. 1.



Catalytic activity of 0·1*N*-$CH_3 \cdot CO_2H$ + x*N*-$CH_3 \cdot CO_2Na$ *in the hydrolysis of ethyl acetate. Reaction velocity* ($v \times 10^7$) *plotted against* p_H.

If the hydrogen-ion concentrations of solutions of the constant-acid series are expressed in terms of the hydrogen-ion concentration of the isocatalytic mixture, such that $n = [\overset{+}{H}]/[\overset{+}{H}]_i$, the equation for the reaction velocity may be written

$$v = k_h[\overset{+}{H}]_i(n + 1/n) + k_m c$$

and for larger values of n this becomes

$$v = nk_h[\overset{+}{H}]_i + k_m c \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The corresponding equation for the minimum velocity is

$$v_i = 2k_h[\overset{+}{\mathrm{H}}]_i + k_m c \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Multiplying (2) by 2 and (3) by n, we obtain by subtraction

$$k_m = (nv_i - 2v)/(n-2)c \quad . \quad . \quad . \quad . \quad (4)$$

The use of equation (4) for the determination of k_m presumes a knowledge of the isocatalytic data, but does not entail measurements of reaction velocity for solutions which contain a much larger proportion of salt than that which is present in the isocatalytic mixture. In this respect, the method is very different from the extrapolation method, and since for various reasons the experimental realisation of the linear portion of the v–x curve is not always possible, the method represented by equation (4) may frequently be found to be useful for the determination of k_m.

Its application in the present case is illustrated by Table II, in which the relevant numbers for the solutions containing relatively small quantities of salt are recorded.

TABLE II.

$c = 0{\cdot}1$. $[\overset{+}{\mathrm{H}}]_i = 8{\cdot}4 \times 10^{-6}$, $v_i = 2{\cdot}5 \times 10^{-7}$.

x.	$[\overset{+}{\mathrm{H}}] \cdot 10^5$.	n.	$v \cdot 10^7$.	$k_m \cdot 10^7$.
0	135	159	81·6	15·0
0·005	34·5	40·5	23·1	14·3
0·015	12·2	14·4	9·1	14·4
0·03	6·15	7·3	5·2	14·8

In spite of the wide variation in the value of the "reduced" hydrogen-ion concentration (n), the numbers under k_m are remarkably concordant, and this may be regarded as further evidence in support of the validity of the general theoretical considerations on which the method of interpreting the results is based. According to this, the catalytic effects associated with acetic acid and its salts in the hydrolysis of ethyl acetate are very similar to those previously met with in the case of the acetone–iodine reaction. The main difference is attributable to the fact that the ratios k_m/k_h and k_a/k_h are much larger for the latter reaction than for the ester hydrolysis. This is also true for the ratio k_{OH}/k_h. The actual values of the ratios are shown in Table III.

TABLE III.

Reaction.	$10^5 \times k_m/k_h$.	$10^5 \times k_a/k_h$.	$10^{-3} \times k_{\mathrm{OH}}/k_h$.	$10^{-6} \times k_{\mathrm{OH}}/k_a$.
(A) Acetone–iodine ...	320	970	43	4·4
(B) Hydrolysis of ethyl acetate ...	24	3·3	1·05	32

According to the above figures k_a/k_h is about 300 times as great for reaction A as for reaction B. This is mainly responsible for the fact that the amount of acetate which must be added to 0·1*N*-acetic acid to reduce the reaction velocity to a minimum is nearly 20 times as great in B as it is in A. On the other hand, k_{OH}/k_a is about 7 times as great in B as it is in A. This explains why the anionic catalytic effect in B is shared by the acetate and hydroxyl ions, although the corresponding effect in A is almost entirely due to the acetate ion. That the nature of the catalysed reaction affects the relative activities of the undissociated acid and the corresponding anion is evident from the value of the ratio k_m/k_a; this is 0·33 in reaction A and 7·2 in reaction B.

Catalytic Effects for Different Reactions and the General Catenary.—Since the catalytic effects associated with the two reactions which have been compared are in agreement with the requirements of the general catalytic catenary (compare this vol., p. 213), according to which the reduced ionic velocity $r = u/u_i$ is connected with the reduced hydrogen-ion concentration, $n = [\overset{+}{H}]/[\overset{+}{H}]_i$, and the reduced p_H value, $\Delta p_H = \log_{10} n$, by the equations

$$r = \tfrac{1}{2}(n + 1/n) = \tfrac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H})$$

these reduced quantities should afford a basis for the comparison of the ionic catalytic effects which are peculiar to a given acid in a series of different reactions. It has, in fact, been shown (this vol., p. 756) that the reduced hydrogen-ion concentration (n_0) of a solution of the pure acid and the corresponding reduced ionic velocity (r_0) are determined solely by the relative magnitudes of the catalytic coefficients and are independent of the concentration and therefore of the degree of ionisation of the acid. The value of n_0 (or r_0) determines the position which must be assigned to a given pure acid on the general catalytic catenary, and this position obviously varies with the nature of the catalysed reaction. For acetic acid, the value of n_0 is 10 when the acid catalyses the acetone–iodine reaction, and about 175 when it catalyses the hydrolysis of ethyl acetate. Such wide variations in n_0 do not, of course, affect the validity of the relations which find expression in the equation of the general catalytic catenary, but they serve to show that the catalytic activity of a given pure acid expressed in terms of that of the corresponding *M.V.* mixture varies very considerably with the nature of the catalysed reaction.

Summary.

Measurements have been made of the catalysing power of acetic acid–sodium acetate mixtures in the hydrolysis of ethyl acetate.

For a fixed concentration of acid, the addition of salt first reduces the velocity, which passes through a minimum, and then increases it according to a linear formula.

The observed reaction velocities can be explained in terms of the joint catalytic effects produced individually by the hydrogen, acetate, and hydroxyl ions and by the undissociated acetic acid.

The connexion between the reaction velocity and the p_H value of the solution is represented very closely by a catenary curve.

The ratios k_a/k_h and k_m/k_h are much smaller for the hydrolysis of ethyl acetate than for the acetone–iodine reaction, and the catalytic catenary is of the compound type.

THE UNIVERSITY, LEEDS. [*Received, July 16th*, 1927.]

CCCXXVIII.—*The Heat of Adsorption of Oxygen on Charcoal. Part II.*

By WILLIAM E. GARNER and DOUGLAS MCKIE.

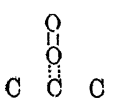
DEBYE and SCHERRER (*Physikal. Z.*, 1917, **18**, 291) concluded from an *X*-ray examination by the powder method that amorphous carbon was merely graphite in a powder form. This conclusion was criticised by Ruff, Schmidt, and Olbrich (*Z. anorg. Chem.*, 1925, **148**, 313), who are of the opinion that amorphous carbon is a true modification which begins to pass into a para-crystalline variety at 1100°, and that the different forms of amorphous carbon are to be attributed to the admixture of varying proportions of graphite and a para-crystalline form. From their investigation, it would appear that the adsorptive powers of charcoal are due to the amorphous form alone.

The energy content of amorphous carbon is 3 Cals./mol. higher than that of graphite. This difference in energy must be associated with structural differences probably extending throughout the body of the carbon. The most probable structure of amorphous carbon, in view of its mode of formation from cellulose or sugars, is that of an interlocking network of carbon chains, which are the degradation products of the original cellulose molecules. With such a structure, adjacent carbon chains will touch at points irregularly along their length. Where contact occurs between carbon atoms of adjacent chains, presumably something analogous to chemical combination has occurred, but there must exist atoms in the body of the carbon the valency forces of which are not fully saturated by neighbouring atoms. The excess of potential energy of amorphous carbon would be expected to lie in such atoms and in those exposed in the capillary surfaces of the charcoal.

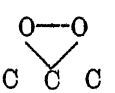
Each of the surface atoms forms part of a chain extending into and rigidly fixed in the body of the carbon. The surface atoms may possess the haphazard distribution of their fellows in the body of the charcoal. Those projecting some distance from the surface are conceivably unsaturated chemically. Birge (*Physical Rev.*, 1926, **28**, 259), from a consideration of results on the heat of vaporisation of carbon and an examination of the molecular spectra of oxygen and the oxides of carbon, concluded that 1 g.-mol. of gaseous carbon contains 141 Cals. more potential energy than carbon in bulk. This value sets the limit for the potential energy of the most active carbon atoms on the surface of charcoal. The potential energy of these atoms will very probably range between 141 Cals. and zero, the former value corresponding with carbon atoms practically in the gaseous state and the latter with atoms almost completely surrounded by neighbouring atoms. The nature of the law of the distribution of energy among the surface atoms is unknown.

The potential energy of the carbon surface should be liberated during chemical changes occurring thereon, *e.g.*, during the adsorption of oxygen. Under the most favourable conditions, the heat of adsorption of this gas should approach a value of the order of 300,000 cals. per g.-mol. of oxygen adsorbed.

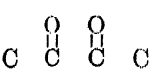
There is some justification for assuming that combination between oxygen molecules and carbon atoms on the surface can take place according to definite stoicheiometrical relationships. This would be the case if electron sharing occurs between the surface and adsorbed atoms. Also, there is the possibility of physical adsorption, the oxygen being held by subsidiary valency forces on the surface. The following simple structural forms may be present on a carbon surface which has adsorbed oxygen (C C C . . . represents the surface):



(I.)



(II.)



(III.)

(I) represents the process of physical adsorption of oxygen in which there is no electron transference or sharing between the atoms. The adsorption is, in this case, a reversible process, and the adsorbed oxygen molecules can be recovered unchanged. (II) and (III) are examples of modes of chemical combination. Desorption of oxygen should occur as carbon dioxide in (II) and as carbon monoxide in (III). Other types of complex may exist, but our object is to present as simple a picture as possible.

Our knowledge of these adsorption complexes is based on (*a*)

the nature of the products obtained on desorption, and (*b*) measurements of heats of adsorption. The products would appear to depend, not only on the temperature of desorption, but also on factors concerning the adsorption process. The amount of oxygen adsorbed by a given mass of charcoal and the temperature at which adsorption occurs are the main factors involved. At low temperatures and high initial gas pressures, the adsorbed gas can be recovered as oxygen on decreasing the pressure or on raising the temperature (Dewar, *Proc. Roy. Soc.*, 1904, *A*, **74**, 122). This form of adsorbed oxygen is represented by (I). The heat of adsorption is very low, about 3 Cals. per mol. of gas adsorbed. If the gas is admitted at low pressures, *e.g.*, 0·01 mm., and at the ordinary or slightly higher temperature, the adsorbed oxygen can be recovered as oxides of carbon (II and III) on raising the temperature. The heat of adsorption under these conditions is much higher. At room temperature, the maximum heat of adsorption is 70 Cals./g.-mol. (Keyes and Marshall, *J. Amer. Chem. Soc.*, 1927, **49**, 156) and rises rapidly with increase in temperature (Blench and Garner, J., 1924, **125**, 1288). At high pressures and at room temperature, the heat of adsorption is only 4 Cals./mol., and the adsorption complexes may be of all three types, (I), (II), and (III). Rhead and Wheeler (J., 1913, **103**, 471) have shown that the complexes formed at 300° break down into carbon dioxide and monoxide at higher temperatures. Type (II), giving dioxide, would appear to be less stable than (III). The maximum evolution of carbon dioxide occurs at approximately 300—400°, and of carbon monoxide at 600—700° (Rhead and Wheeler, *loc. cit.*). Since both carbon dioxide and monoxide are liberated over a wide range of temperatures,* the forces holding the molecules of the gas on the surface cannot be uniform from molecule to molecule. This is what would be anticipated were the surface adsorbing oxygen truly amorphous.

An investigation continuing the work of Blench and one of us and using a more refined technique has thrown additional light on the nature of the adsorption complexes. The detailed experimental method will be described in a later paper. It will be sufficient to state here that the adsorption was carried out in a vacuum calorimeter of known water equivalent and the rise in temperature measured by means of a thermocouple. The heat of adsorption varies with the initial gas pressure, *i.e.*, with the amount of oxygen adsorbed, in a curious manner. This will be seen by combining the results of McKie and those of Keyes and Marshall (Table I). Although the latter authors measured the heats of adsorption by a

* Only a fraction of the complexes breaks down when the carbon is heated over a range of 50°.

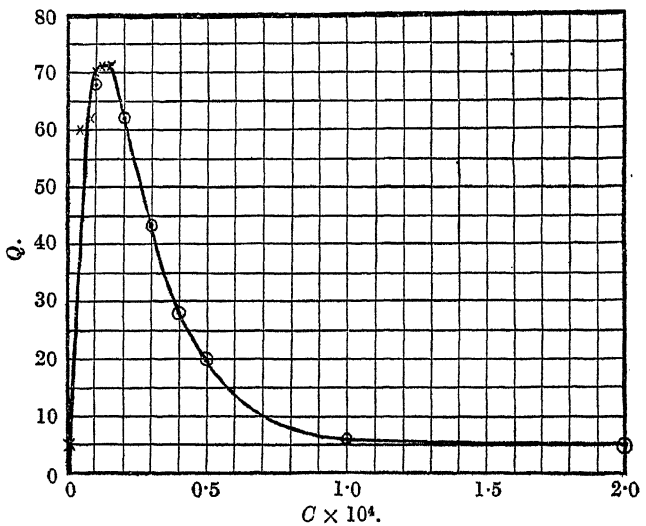
different experimental method (by the ice calorimeter), their results agree very well with those of McKie. Charcoals with practically the same activity must have been used in both series of experiments.

TABLE I.

Heat of adsorption (Cals./mol.).

$C \times 10^4$.	Q per mol. of O_2 at 18° (McKie).	$C \times 10^4$.	Q per mol. of O_2 at 0° (Keyes and Marshall).
0·001 to 0·006	5	0·1	67·9
0·04	60	0·2	61·9
0·08	62	0·3	43·5
0·10	70	0·4	27·9
0·12	71	0·5	20·1
0·15	71	1·0	5·8
		2·0	5·1
		4·0	4·4

FIG. 1.



C represents the number of g.-mols. of oxygen adsorbed per g. of charcoal, and Q is the molar heat of adsorption.* Different charcoals show the same maximum value of Q, although this does not necessarily occur at the same value of C. The results are plotted in Fig. 1. There is a sharp rise in the heat of adsorption up to a maximum value of 70 Cals. and then a slower fall down to 4 Cals. as the density of adsorbed oxygen increases. A similar curve has been obtained by Kistiakowski (*Proc. Nat. Acad. Sci.*, 1927, **13**, 1) for the heat of adsorption of hydrogen on nickel.

* The oxygen admitted is almost completely adsorbed at a surface density of $C = 0$ to $C = 0{\cdot}1 \times 10^{-4}$.

The internal area of the charcoal used in the above experiments has been determined by measuring the adsorption isotherms of straight-chain alcohols on the charcoal (area = 66 m.^{2} per g.) (Garner, McKie, and Knight, *J. Physical Chem.*, 1927, **31**, 641). At the maximum of Fig. 1, only 1/140 of the carbon atoms are covered with oxygen, so that the range of figures given in Table I refers only to the formation of an incomplete unimolecular film of oxygen molecules on the surface.

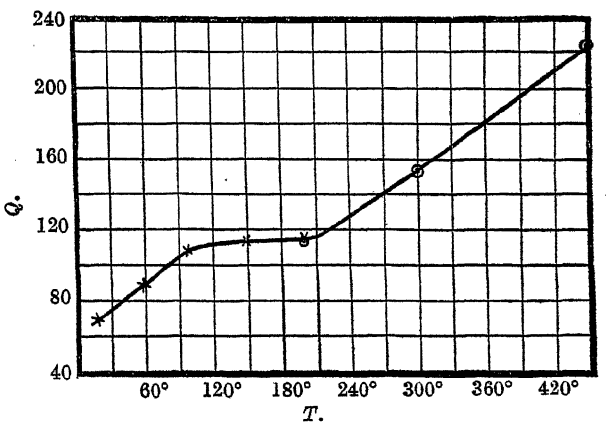
The heat of adsorption varies with the temperature. Values are shown in Table II for $C = 0{\cdot}1 \times 10^{-4}$. The agreement between

TABLE II.

Relation between heat of adsorption and temperature.

Temperature	18°	57°	100°	150°	200°	300°	450°
Q (McKie)	70	91	108	114	116	—	—
Q (Blench and Garner)	—	—	—	—	115	154	224

FIG. 2.



the values of McKie and those of Blench and Garner at 200° is probably a coincidence, since the latter were not so accurately determined as the former.

Fig. 2 brings out the nature of the rise in Q. This approaches a constant value between 100° and 200° and then rises rapidly. In the interpretation of these results, it is necessary to bear in mind that the accuracy of the values decreases with increase in temperature. Up to 100°, only negligible amounts of carbon dioxide are produced on admitting oxygen to the charcoal, but at higher temperatures this gas is liberated in increasing amounts. At 450°, more than 30% of the oxygen combining with the surface is liberated as dioxide. This makes the deduction of the heat of

adsorption uncertain. Nevertheless, we believe the general trend of the curve to be correct.

The temperature coefficient of the heat of adsorption is too great to be accounted for by changes in the specific heats of the resultants and reactants. It must be due to a change in the type of complex with the temperature. The heat of adsorption approaches a constant value at 100—200°. This suggests that the type of complex which is formed does not undergo much change over this range of temperatures. Below 100°, at least two types must be present, one of which gives place to the other on increase in temperature. This change is nearly complete at 100°. It is highly probable that at this temperature only one structural form is present. This cannot be (I), but is very probably (II). The experiments of Rhead and Wheeler on the decomposition of the complex indicate that this is the case; carbon dioxide is the main product of desorption at 300—400°. If this is so, then the rise in Q above 200° must be ascribed to the formation of (III). If Q were very large for type (III), then a high temperature would be necessary before desorption could be brought about. This is supported by the fact that the maximum evolution of carbon monoxide does not occur until 600—700° is reached.

Although the heat of adsorption obtained between 100° and 200° is believed to be that of type (II), it is not suggested that this heat is other than an average value. Owing to the varying potential energy of the carbon atoms on which the complex is formed, a range of heats of adsorption for type (II) would be expected. This would account for the wide range of temperatures over which the complex is broken down to give carbon dioxide.

Returning to Fig. 1, we are met with greater difficulties in interpretation. The decrease in Q as the amount of gas adsorbed increases is undoubtedly due to the increasing predominance of molecularly adsorbed oxygen (I). The low heat, and the fact that from such charcoals oxygen may be recovered, requires that this be the case. The occurrence of a maximum value and the fall at very low surface concentrations afford an interesting problem for the complete solution of which there are not sufficient data. If it be assumed that the fall is due to the occurrence of physical adsorption at very low pressures, it must also be assumed that the oxygen is very tightly bound to the surface, which occurs very rarely for physical adsorption. At $C = 0{\cdot}01 \times 10^{-4}$ g. mol./g., only 1 in every 1400 of the surface carbon atoms is covered, and these will be the most unsaturated of the surface atoms. If a physical complex is formed, it may thus be comparatively stable.

An alternative and preferable explanation would be that, at

very low pressures and surface densities, an active form of type (II) is formed which only slowly liberates its internal energy as heat or radiation. The liberation of energy may occur so slowly that we cannot measure it by our methods. In support of this, it may be mentioned that the rate of liberation of heat is slower when $C = 0{\cdot}04 \times 10^{-4}$ than when $C = 0{\cdot}1 \times 10^{-4}$. It is probable that an activated form of type (II) would give up its energy if struck by an oxygen molecule, and this may be the explanation of the increased heat of adsorption as the density of the gas above the carbon increases.

Support for this view was found on studying the adsorption of mixtures of oxygen and nitrogen. Nitrogen is adsorbed when admitted together with oxygen in greater amounts than if admitted either to a bare carbon surface or to a surface on which oxygen has been adsorbed. The gas is not, however, held so firmly as either oxygen or nitrogen which has been adsorbed on a bare surface; it evaporates when the pressure is lowered. An unstable carbon, oxygen, and nitrogen complex is formed. The complexes formed when nitrogen is admitted after oxygen are much more stable (compare *Trans. Faraday Soc.*, 1926, **22**, 459).

These results indicate that the adsorbed oxygen molecules are in a chemically active state immediately after formation, and that this activity is lost on standing. They support the view expressed above that the initial portion of the curve in Fig. 1 is due to the formation of a complex of type (II), which has retained a large portion of its heat of formation. A similar explanation can also be given for Kistiakowski's curve (*loc. cit.*).

Summary.

The heat of adsorption of oxygen on charcoal varies with the amount of oxygen adsorbed per g. of charcoal. A maximum value (70 Cals.) was obtained when the number of g.-mols. of oxygen adsorbed per g. of charcoal was $1{\cdot}5 \times 10^{-5}$. The maximum heat of adsorption increases rapidly with increase in temperature, approaching 115 Cals. between 100° and 200°. It rises again from 200° to 450°.

The results have been discussed with regard to the light they throw on the chemical constitution of the C_xO_y complex.

One of us (D. McK.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant.

THE RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, August 5th*, 1927.]

CCCXXIX.—*The Interaction of Bromine with Acetic Anhydride. Part II.*

By KENNEDY JOSEPH PREVITÉ ORTON, HERBERT BEN WATSON, and HUBERT IVOR HUGHES.

IT has been stated by Orton and Jones (J., 1912, **101**, 1722), and subsequently by W. H. Gray (Thesis, Univ. of Wales, 1913) and by Orton, Watson, and Bayliss (Part I, J., 1923, **123**, 3081), that pure acetic anhydride is unattacked by halogens at the ordinary temperature when light is completely excluded. The anhydride used by these investigators was obtained by fractional distillation of Kahlbaum's acetic anhydride "free from homologues," and their observation does not appear to find confirmation in the results of earlier workers (Gal, *Ann. Chim. Phys.*, 1862, **66**, 187; Urech, *Ber.*, 1880, **13**, 1687; Lapworth, J., 1904, **85**, 40). The stability to bromine of specimens of acetic anhydride of varied origin and purified by different methods has now been examined; in every case reaction occurs, and it appears probable that the material employed by the previous workers contained a trace of some inhibitor which was not removed by fractionation. A search for possible inhibitors has revealed the fact that introduction of quinoline in minute quantity prevents the reaction from proceeding to any perceptible extent during a long interval of time (with bromine = 0·25*M* and quinoline = 0·006*M*, no measurable amount of bromine reacted in 93 hrs.); moreover, acetic anhydride containing a trace of quinoline is still stable to bromine after fractionation. After this "latent period," reaction proceeds at a measurable rate, but the disappearance of bromine is much slower than when pure anhydride is employed; the retardation at this stage is probably to be attributed to the presence of a hydrobromide of quinoline, for a similar retardation is produced by introduction of a trace of sodium or potassium bromide or of certain other salts. Sodium acetate exerts an influence which is similar to but not as powerful as that of quinoline (with $Br_2 = 0{\cdot}26M$ and $NaC_2H_3O_2 = 0{\cdot}005M$, no fall of titre after 17 hrs.), whilst pyridine, dimethylaniline, triethylamine, diethylamine, *iso*quinoline, ammonium acetate, methylamine, and ethylamine are less effective. Addition of a trace of nitric acid or of acetyl nitrate is accompanied by an extremely powerful inhibition (compare Gray, *loc. cit.*); the effect of the former is probably due to acetyl nitrate formed by reaction of the nitric acid with the anhydride, for the bromination of propionic anhydride (which is similar to that of acetic anhydride, but considerably

slower) is inhibited by acetic anhydride and nitric acid in conjunction, but not by nitric acid alone.

The speed of interaction of bromine with acetic anhydride is now found to be greatly influenced by the concentration of the halogen. The course of the reaction indicates autocatalysis, and introduction of acetyl bromide (one of the products, Gal, Urech, *locc. cit.*) causes a considerable acceleration. The effect of acetyl bromide is identical with that of hydrogen bromide at equimolar concentration, indicating that the halogen acid reacts all but completely with the anhydride, $(CH_3\cdot CO)_2O + HBr = CH_3\cdot COBr + CH_3\cdot CO_2H$, as has been shown by an aspiration method. Introduction of propionyl or benzoyl bromide brings about an acceleration identical with that produced by acetyl bromide at the same concentration. These facts recall the bromination of carboxylic acids (Watson, J., 1925, **127**, 2067), and a similar series of changes of the following type is indicated:

$$CH_3\cdot COBr + Br_2 = CH_2Br\cdot COBr + HBr \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$(CH_3\cdot CO)_2O + HBr \rightleftarrows CH_3\cdot COBr + CH_3\cdot CO_2H \quad . \quad . \quad . \quad . \quad (2A)$$

$$(CH_3\cdot CO)_2O + CH_2Br\cdot COBr \rightleftarrows CH_2Br\cdot CO\cdot O\cdot CO\cdot CH_3 + CH_3\cdot COBr \quad . \quad . \quad . \quad (2B)$$

$$CH_3\cdot CO_2H + CH_2Br\cdot CO\cdot O\cdot CO\cdot CH_3 \rightleftarrows (CH_3\cdot CO)_2O + CH_2Br\cdot CO_2H \quad . \quad . \quad . \quad . \quad (3)$$

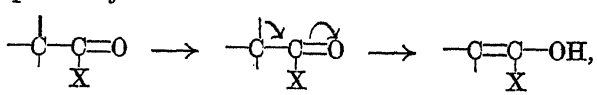
When the bromide of another acid is added initially, these reactions will be preceded by

$$(CH_3\cdot CO)_2O + R\cdot COBr \rightleftarrows CH_3\cdot CO\cdot O\cdot CO\cdot R + CH_3\cdot COBr, \text{ or}$$
$$(CH_3\cdot CO)_2O + 2R\cdot COBr \rightleftarrows (R\cdot CO)_2O + 2CH_3\cdot COBr \quad . \quad . \quad (4)$$

That acetic anhydride can react with acid bromides in this manner is demonstrated by distilling a quantity of the anhydride with either bromoacetyl or benzoyl bromide, whereby a good yield of acetyl bromide is obtained; it is not suggested that reaction (3), which is analogous to the reactions of acids with anhydrides observed by Kaufmann and Luterbacher (*Ber.*, 1909, **42**, 3483), proceeds to any great extent under the conditions of the authors' experiments, in which the acetic anhydride was always in great excess. In the above series of reactions the rate of disappearance of bromine will be $dx/dt = k(a-x)[\text{AcBr}]$, where a is the initial concentration of bromine. If the acetyl bromide be present in excess, the reaction will be of the first order; values of $k_1 = 1/t \cdot \log_e a/(a-x)$, however, were not constant. If the bromine also reacts with the enolic form of the anhydride (this form being produced slowly and reacting with halogens rapidly; compare Part I), the rate of disappearance of bromine will be $dx/dt = k(a-x)[\text{AcBr}] + k'[\text{Ac}_2\text{O}]$, where x is

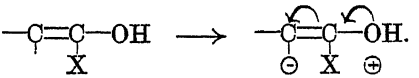
the total amount of the halogen which reacts in time t. In the case when both acid bromide and anhydride are in excess, this reduces to $dx/dt = C(a - x) + C' = C(a - x + P)$, where $C' = CP$, which on integration becomes $C = 1/t \cdot \log_e (a + P)/(a + P - x)$. Constant values of C were obtained by use of this expression. The observed facts are thus interpreted by supposing that the reaction proceeds mainly through a series of changes involving the bromination of the acid bromide, but also to a small extent through the enolised anhydride. Addition of a small quantity of sulphuric acid, ferric chloride,* or stannic chloride results in a marked increase in the rate of disappearance of bromine (compare Part I); their effect probably consists in an acceleration of the enolisation of the anhydride. Acetyl chloride (or added hydrogen chloride), trichloroacetic acid, and monobromoacetic acid are without appreciable effect. When pure anhydride is used, pure dry iodine is now found to be a catalyst, but iodine bromide (added as such) and iodine chloride are more effective, the former being a particularly good catalyst.

According to the hypothesis of activation by electronic displacement (Allan, Oxford, Robinson, and Smith, J., 1926, 401; Ingold and Ingold, *ibid.*, p. 1310) there will be but little tendency for a proton to become loosened from the methyl group of acetic acid, for the carboxyl group is "self-contained" (Ray and Robinson, J., 1925, **127**, 1618); adjustment of the covalencies of the carbonyl carbon atom of acetic anhydride, however, will take place to a smaller extent, since the singly-linked oxygen is conjugated on both sides (compare Lea and Robinson, J., 1926, 411), whilst with acetone and acetyl bromide no such adjustment is possible. In the three compounds last mentioned, therefore, loosening of a proton will occur, and will be most marked in acetyl bromide owing to the "polar effect" of the bromine atom (Baker and Ingold, J., 1926, 2466). The loosened proton is attracted towards the negatively charged carbonyl oxygen, and enolisation takes place (in preference to direct substitution by a reagent, as is shown by the dynamics of the bromination of acetone; Lapworth, *loc. cit.*). The sequence $CH_3{\cdot}COBr > (CH_3)_2CO > (CH_3{\cdot}CO)_2O > CH_3{\cdot}CO_2H$ is thus obtained for velocity of enolisation. The series of changes up to this point may be written



* Using pure anhydride, the authors have failed to confirm the violet colour ascribed in Part I (p. 3090) to solutions of anhydrous ferric chloride. Such solutions are brown in colour.

and on activation of the enolide



The activated enolide will react with bromine at the negatively charged carbon atom, the products being the monobrominated ketonic derivative and hydrogen bromide. In acetyl bromide, the activation of the enolide will be opposed by the polar effect of the bromine atom, and hence *rapid* enolisation will be followed by a comparatively slow reaction with bromine (compare Watson, *loc. cit.*, p. 2075), whilst in acetone and acetic anhydride slow enolisation is followed by rapid reaction with the halogen. These considerations lead to the idea suggested originally by Lapworth (*loc. cit.*) that the bromination of carbonyl compounds in general is preceded (provided an α-hydrogen atom is present) by conversion into the enolic form; it is not necessary, however, to assume the formation of an intermediate dibromide which immediately loses hydrogen bromide, nor has such a dibromide been isolated. This scheme correlates the results of Lapworth and others on the bromination of ketones and aldehydes, those of Watson on the bromination of carboxylic acids, and also those described in the present paper.

Experimental.

The velocity measurements were carried out by withdrawal at suitable intervals of 2 (± 0·01) c.c. of the reaction mixture, addition to aqueous potassium iodide, and titration of the iodine liberated with *N*/10-thiosulphate. Unless otherwise stated, titres are expressed as c.c. of *N*/10-thiosulphate, and time in minutes. Temperature throughout = 25°.

Reaction of Bromine with Different Specimens of Acetic Anhydride.—The anhydride was fractionated through an eight-pear stillhead, and the bromine (B.D.H. "A.R." quality) was purified as described by Watson (*loc. cit.*, p. 2076).

Br_2 = 0·25—0·27*M*, initially; mol. ratio Ac_2O/Br_2 = 40.

	Fall in titre after (mins.)							
Initial titre.	20.	30.	40.	50.	60.	70.	80.	90.
Kahlbaum's acetic anhydride "free from homologues" (post-war).								
10·30	1·45	2·80	4·52	5·90	7·10	8·05	8·72	9·20
Hopkin and Williams's "Reagent" acetic anhydride (post-war). (Mean of results for ten specimens.)								
10·38 (±0·25)	1·32	2·65	4·00	5·42	6·65	7·20	8·38	8·98 (±0·5)
British Drug Houses "A.R." acetic anhydride (post-war).								
10·45	1·70	3·45	4·85	6·32	7·60	8·42	9·05	9·48

Effect of Purification of Bromine.—Method 1 as above: results are the mean of those in previous table. Method 2: bromine distilled from potassium bromide and zinc oxide (compare Stas, *Mem. Acad. Belgique*, 1865, **35**, 3; West, J., 1924, **125**, 1279), then dried over quick-lime and distilled in an all-glass apparatus. Method 3: bromine distilled from potassium bromide and zinc oxide, then washed with distilled water and dried under concentrated sulphuric acid, separated, and distilled from a little barium carbonate.

	Initial titre.	Fall in titre after (mins.) 20.	30.	40.	50.	60.	70.	80.	90.
Method 1 ...	10·38	1·48	2·98	4·45	5·62	7·12	7·88	8·72	9·22
Method 2 ...	10·40	1·10	2·28	3·65	5·12	6·35	7·35	8·20	8·82
Method 3 ...	10·28	0·90	1·80	3·05	4·55	5·75	6·85	7·75	8·45
Untreated ...	10·15	1·35	2·70	4·22	5·70	6·82	7·78	8·45	9·00

Effect of Purification of Acetic Anhydride by Different Methods.—Specimens of the anhydride were distilled from phosphorus pentoxide (method 1), potassium permanganate (2), or chromic anhydride (3); allowed to stand for 48 hours over pure anhydrous sodium acetate and then distilled (4), refluxed for 12 hours over sodium acetate and then distilled (5), and treated with 0·1% by volume of bromine, allowed to stand until colourless, refluxed for 6 hours over sodium acetate, and distilled (6). In each case, the anhydride was fractionated both before and after the treatment described.

	Initial titre.	Fall in titre after (mins.) 20.	30.	40.	50.	60.	70.	80.	90.
Method 1 ...	10·52	1·42	3·60	5·25	6·68	7·78	8·60	9·20	9·60
Method 2 ...	10·55	1·05	2·28	3·78	5·20	6·55	7·60	8·40	9·10
Method 3 ...	10·45	1·38	3·02	4·65	6·05	7·25	8·22	8·92	9·40
Method 4 ...	10·50	1·70	3·25	4·80	6·45	7·60	8·52	9·12	9·55
Method 5 ...	10·45	1·68	3·05	4·65	6·08	7·22	8·12	8·80	9·30
Method 6 ...	10·25	1·60	3·25	4·88	6·20	7·95	8·22	8·50	9·30

Effect of varying Bromine Concentration.

Conc. of bromine.	Initial titre.	Fall of titre after (mins.) 20.	30.	40.	50.	60.	70.	80.	90.
0·474*M*	18·95	6·75	11·28	14·18	16·12	17·32	18·10		
0·260*M*	10·38	1·48	2·98	4·45	5·62	7·12	7·88	8·72	9·22
0·148*M*	5·92	0·35	0·70	1·10	1·68	2·28	2·82	3·38	3·85

Effect of Inhibitors.—The substances used were the purest specimens obtainable, further purified in many cases by the usual methods.

Substance added.	Conc. (M) ($\pm$0·001).	Initial titre.	Time (mins.) required for fall in titre of 2 c.c.	6 c.c.	9 c.c.
Quinoline	0·006	10·25	6960	7080	7320
Sodium acetate	0·005	10·55	1200	1320	1530
„ „	0·0025	10·42	555	630	795
„ „	0·0005	10·25	45	90	135
Pyridine	0·005	12·75	495	585	630
Dimethylaniline	0·005	9·82	255	495	735
Triethylamine	0·005	10·75	165	375	660
Diethylamine	0·005	10·35	105	210	360
*iso*Quinoline	0·009	10·12	90	315	—
Ammonium acetate	0·005	10·45	60	105	150
Methylamine	0·005	10·30	60	135	240
Ethylamine	0·005	10·42	45	105	195
Sodium bromide	0·005	10·15	285	525	840
Potassium bromide	0·0055	10·35	240	480	780
Sodium chloride	Trace	10·35	180	510	900
Sodium benzenesulphonate	„	10·25	60	120	300

Effect of Nitric Acid and of Acetyl Nitrate.—A solution of pure nitric acid (prepared from pure potassium nitrate and pure sulphuric acid) in acetic acid (m. p. 16·4°) was freed from nitrous acid by aspiration with purified air (Gray, *loc. cit.*) and estimated in a Lunge nitrometer. 0·05 C.c. of this solution and 0·3 c.c. of bromine were made up to 25 c.c. at 25° with acetic anhydride, giving HNO_3 = 0·003M. The titre of 2 c.c. of this solution was as follows :

Time (days)	0	3	5	7	10	17
Titre (c.c.)	10·55	10·40	10·40	10·25	9·95	9·55

0·1 C.c. of acetyl nitrate, prepared as described by Pictet and Khotinsky (*Compt. rend.*, 1907, **144**, 210), b. p. 27°/30 mm., and 0·3 c.c. of bromine were made up to 25 c.c. with acetic anhydride. Titre of 2 c.c. as follows :

Time (days)	0	14
Titre (c.c.)	11·38	11·15

Propionic anhydride, prepared by fractionation of Kahlbaum material (b. p. 166°/771·5 mm.), reacted with bromine as follows :

Time (hrs.)	0	2	3	5	7	10
Titre (c.c.)	9·32	9·12	8·18	7·75	7·10	6·40

With propionic anhydride, to which a little nitric acid (0·03M) had been added, a titre of 10·05 c.c. fell to 2·85 c.c. in 48 hours. When acetic anhydride (0·03M) and nitric acid (0·03M) were both added, a titre of 10·98 c.c. fell only to 10·95 c.c. in 5 days.

Effect of Catalysts and Other Substances.—Solutions of hydrogen bromide and hydrogen chloride in the anhydride, pure acetyl chloride, and pure acetyl, benzoyl, and propionyl bromides were obtained as described by one of us (Watson, *loc. cit.*). The sulphuric acid, ferric chloride, and stannic chloride were purified by distillation

or sublimation, and pure iodine and iodine bromide were prepared as described in Part I, p. 3094.

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (mins.) 10.	20.	30.	40.	50.	60.	70.
AcBr	0·024	10·38	1·32	3·12	4·90	6·52	7·68	8·52	9·18
HBr	0·024	10·25	1·45	3·25	5·15	6·58	7·68	8·55	9·15
BzBr	0·024	10·40	1·42	3·32	5·18	6·75	7·82	8·65	9·30
AcBr	0·109	11·30	2·88	5·52	7·48	8·92	9·80	10·40	
PrBr	0·109	11·50	2·92	5·62	7·62	9·02	9·92	10·58	
BzBr	0·109	11·10	2·78	5·45	7·38	8·78	9·70	10·22	
AcBr	0·240	10·28	3·52	6·32	8·05	9·00	9·65		
HBr	0·240	9·90	3·68	6·35	7·95	8·85	9·40		
HCl	0·027	10·10	0·38	1·25	2·92	4·50	5·85	7·05	7·95
HCl	0·270	10·15	0·50	1·55	3·25	4·85	6·20	7·35	8·25
HCl	0·540	10·28	0·58	1·82	3·35	5·08	6·50	7·60	8·35
AcCl	0·270	10·15	0·25	1·25	2·88	4·42	5·85	7·02	7·85
AcCl	0·540	10·22	0·75	1·72	3·10	4·68	6·02	7·08	8·08
$CCl_3{\cdot}CO_2H$ ...	0·009	10·50	0·45	1·40	2·95	4·70	6·15	7·40	8·22
$CCl_3{\cdot}CO_2H$ ...	0·048	10·25	0·40	1·32	2·85	4·52	5·92	7·10	8·00
$CH_2Br{\cdot}CO_2H$	0·147	10·40	0·50	1·65	3·10	4·85	6·15	7·38	8·22
$CH_3{\cdot}CO_2H$ ...	0·450	10·12	0·38	1·80	3·30	5·10	6·58	7·52	8·40
H_2SO_4	0·001	10·30	1·00	2·95	5·15	6·78	8·18	9·18	9·82
H_2SO_4	0·002	10·20	1·28	3·40	5·75	7·55	8·98		

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (mins.) 10.	15.	20.	25.	30.	35.
$FeCl_3$	0·0012	10·22	1·25	2·68	4·45	6·10	7·85	9·08
$FeCl_3$	0·0024	10·40	3·18	6·50	9·40	10·22		
$SnCl_4$	0·0029	10·18	0·78	1·60	3·38	5·40	7·70	9·20
I_2	0·0030	10·02	1·72	3·92	6·15	8·22	9·75	9·95
I_2	0·0060	9·95	3·98	7·60	9·82			
IBr	0·0006	10·40	2·00	3·90	6·25	8·42	9·80	
IBr	0·0012	10·25	3·80	6·90	9·15	10·00		
IBr	0·0060	9·55	9·52					
ICl	0·0006	10·28	0·65	1·42	2·50	3·82	5·28	6·68
ICl	0·0060	10·32	5·10	9·85				

Examination of a Solution of Hydrogen Bromide in Acetic Anhydride.—The solution was prepared in the same way as those employed in the velocity measurements. A known volume was placed in a bubbler standing in a thermostat at 25°, and a measured volume of pure, dry air was aspirated through this solution and then into standard alkali; the excess of alkali was determined by titration, and the bromide estimated as silver bromide. The amounts of acetic anhydride and acetic acid aspirated over were obtained by blank experiments under identical conditions, the proportion of acetic acid in the mixture being calculated from the equation $HBr + (CH_3{\cdot}CO)_2O = CH_3{\cdot}COBr + CH_3{\cdot}CO_2H$. If the vapour aspirated into the alkali contained acid bromide and no hydrogen bromide, the results would give Mols. acid/Mols. bromide = 2. The mean of two experiments was as follows: Conc. of HBr = 1·41*M*. 500 C.c. of air aspirated through 35 c.c. of this solution in 10 mins. Alkali neutralised = 21·20 c.c. of *N*/20. Alkali equivalent

to Ac_2O and HAc aspirated over = 4·95 c.c. (from blank expt.). Alkali equivalent to HBr or AcBr aspirated over = 16·25 c.c. Wt. of AgBr = 0·0766 g. Hence, mol. acid aspirated over = 0·000812, and mol. bromide = 0·000407. Mol. acid/mol. bromide = 1·99. Applied to other similar solutions, the method gave the following results: Solution of acetyl chloride in acetic anhydride, mol. acid/mol. chloride = 1·98; solution of hydrogen chloride in acetic acid, mol. acid/mol. bromide = 0·98.

Reaction of Acetic Anhydride with Acid Bromides.—Acetic anhydride and bromoacetyl bromide in molar proportion were slowly distilled in an all-glass apparatus; a considerable quantity of liquid distilled at 76—79°/760·9 mm.; this fraction was added to water and the bromine precipitated as silver bromide, giving Br, 63·75 (calc. in AcBr: Br, 65·04%); a smaller fraction distilled at 137—138°, smelt strongly of acetic anhydride, and was probably a mixture of the anhydride with unchanged bromoacetyl bromide (%Br as COBr, 26·05; %Br as COBr in bromoacetyl bromide, 39·6). A fraction of high b. p. remained, probably $(CH_2Br{\cdot}CO)_2O$, which is formed when the mixed anhydride, $CH_2Br{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3$, is distilled (Naumann, *Annalen*, 1864, **129**, 273). Benzoyl bromide (2 mols.) was distilled with acetic anhydride (1 mol.); a large fraction, collected at 77—82°/775 mm., gave %Br as COBr, 65·36; from the liquid remaining some benzoic anhydride (m. p. 40°) and benzoic acid were obtained.

Reaction of Bromine with Acetic Anhydride and Excess of Acetyl Bromide.—In both experiments, $Ac_2O = 9{\cdot}067M$, $AcBr = 1{\cdot}898M$, $P = 0{\cdot}01125$. Titre in c.c. of $N/50$-thiosulphate.

I. $a = 0{\cdot}0887M$.			II. $a = 0{\cdot}0294M$.		
Time.	Titre.	C.	Time.	Titre.	C.
0	17·75		0	5·88	
3	13·35	0·0827	6	2·80	0·0793
7	9·10	0·0808	9	1·70	0·0801
9	7·45	0·0803	14	0·35	0·0813
16	3·32	0·0798			
	Mean	0·0809		Mean	0·0802
	k =	0·0426		k =	0·0423

Average value of $k = 0{\cdot}04245$, giving $C' = 0{\cdot}000906$, $k' = 0{\cdot}0001$.

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UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

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CCCXXX.—*On the Photobromination of* cyclo*Hexane.*

By Basil John Wood and Eric Keightley Rideal.

The photochemical bromination of *cyclo*hexane vapour has been studied by Pusch (*Z. Elektrochem.*, 1918, **24**, 336) and Noddack (*ibid.*, 1921, **27**, 359), who showed that approximately one molecule of bromine was removed for each quantum of light absorbed. The reaction appeared to be the simplest case of photobromination, for there was no evidence of chain formation as in the bromination of toluene, stilbene, cinnamic and tartaric acids, and possibly hydrogen.

The majority of these photobrominations possess marked temperature coefficients, a general interpretation for which has been given by Pratolongo (*Gazzetta*, 1918, **48**, i, 121) and Tolman (*J. Amer. Chem. Soc.*, 1923, **45**, 2285). The existence of a temperature coefficient is believed to be an indication that only those bromine molecules already excited, presumably thermally, to a definite sub-level are capable of becoming excited to a reacting level on absorption of a quantum of the monochromatic radiation employed. The existence of a temperature coefficient for this reaction would clearly be incompatible with the conclusions of Pusch and of Noddack, and the reaction is now shown, in fact, to possess no temperature coefficient for the mercury green line.

In the bromination of hydrogen (Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, 1924, **114**, 208) and of stilbene, cinnamic acid, and potassium oxalate (Berthoud, *Trans. Faraday Soc.*, 1925, **21**, 557; *Helv. Chim. Acta*, 1924, **7**, 318; see also Ghosh and Purkayestha, *J. Indian Chem. Soc.*, 1926, 261), the rate of reaction is claimed to be proportional to the square root of the light intensity and thus to indicate that the reaction involves the formation of bromine atoms according to the reaction

$$Br_2 + h\nu \longrightarrow 2Br \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Berthoud (*loc. cit.*) suggests the following mechanism

$$A + Br \longrightarrow ABr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$ABr + Br_2 \longrightarrow ABr_2 + Br \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2ABr \longrightarrow 2A + Br_2 \text{ or } ABr_2 + A \quad . \quad . \quad . \quad . \quad (4)$$

and deduces the relationships $d[ABr_2]/dt = kI^{\frac{1}{2}}[Br_2]$ or $kI^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}$, respectively, for total or weak absorption of the active radiation, both rates being independent of the concentration of the acceptor. It is difficult to understand how the rate of a photochemical reaction involving bromine atoms with a high primary photochemical efficiency can vary with the square root of the light intensity. If

we equate the rate of formation of bromine atoms by (1) and (3) to their rate of removal by (2) and by the following reactions

$$ABr + Br \longrightarrow ABr_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$2Br \longrightarrow Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we obtain

$$2kI_0[Br_2] + k_3[ABr][Br_2] = k_2[A][Br] + k_5[ABr][Br] + k_6[Br]^2.$$

The reaction rate is then

$$d[ABr_2]/dt = k_5[ABr][Br] + k_4[ABr]^2 + k_3[ABr][Br_2].$$

It is clear that this rate is not proportional to the square root of the light intensity unless the rates of the various methods by which ABr_2 is formed can be considered as negligibly small in comparison with the reaction rate $2Br \longrightarrow Br_2$, *i.e.*, with a reaction of low photochemical efficiency.

If the reaction is not a chain mechanism, we can, following Berthoud, represent it on the atomic view as the sequence of reactions (1), (2), (5), and (6). As the concentration of the bromine atoms is small, we can equate their rate of formation at any instant to their rate of removal, thus, $d[Br]/dt = 2kI_0[Br_2] - k_2[A][Br] - k_5[ABr][Br] - k_6[Br]^2 = 0$. Similarly, since [ABr] is small, $k_2[A][Br] = k_5[ABr][Br]$; moreover, $d[ABr_2]/dt = k_5[ABr][Br]$. For weak absorption of active radiation we thus obtain

$$d[ABr_2]/dt = kI_0[Br_2] - k_6[Br]^2/2 = kI_0[Br_2],$$

since [Br] is assumed to be small.

On this view, the reaction velocity will again be proportional to the light intensity unless but a small fraction of the bromine atoms is removed by the acceptor, in which case the photochemical efficiency is small, and the reaction velocity will be dependent on the concentration of the acceptor.

If the reaction takes place between the acceptor and excited bromine molecules rather than atoms, we obtain for the rate of production of these molecules

$$d[Br_2']/dt = kI_0(1 - e^{a[Br_2]d}),$$

where a is the extinction coefficient and d the thickness of the absorption layer. If τ be the life of an excited bromine molecule and T the time between successive collisions of the excited molecule and the acceptor, the rate of production of the reaction product is (compare Turner, *Physical Rev.*, 1924, **23**, 464)

$$\begin{aligned} d[ABr_2]/dt &= kI_0(1 - e^{-a[Br_2]d})\tau/(T + \tau) \\ &= kI_0[Br_2]\tau/(T + \tau) \end{aligned}$$

for weak absorption. It is clear that this will be independent of the concentration of the acceptor if τ be large compared with T. Since τ is of the order of 10^{-8} second (possibly larger according to Eggert, *Physikal. Z.*, 1923, **24**, 504), we should anticipate that the reaction velocity will not be affected by the concentration of the acceptor until this has fallen to a pressure such that T becomes comparable with τ; this pressure can be calculated from the kinetic gas theory to be only some 0·3 mm. Hg in the case of *cyclo*hexane. Thus, if the primary photochemical action be either the formation of an excited bromine molecule or a dissociation into atoms, the reaction rate would be independent of the concentration of the acceptor except at very low pressures. We would also conclude that for weak light absorption the reaction velocity for the bromination of *cyclo*hexane would be strictly proportional to the light intensity, a view confirmed by experiment.

Finally, it is well known that bromination of many substances in solution is greatly affected by oxygen, which acts as an inhibitor. It was decided to investigate this effect in the case of *cyclo*hexane, because such a quantitative study would give information on the mechanism of the bromination process. The most probable hypothesis is that the reaction proceeds through an excited molecule in the following steps:

$$\mathrm{Br_2} + h\nu \longrightarrow \mathrm{Br_2'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\text{A})$$

$$\mathrm{C_6H_{12}} + \mathrm{Br_2'} \longrightarrow \mathrm{C_6H_{12}Br_2'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathrm{C_6H_{12}Br_2'} \longrightarrow \mathrm{C_6H_{11}Br'} + \mathrm{HBr} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or $$\mathrm{C_6H_{12}Br_2'} + \mathrm{O_2} \longrightarrow \mathrm{C_6H_{12}} + \mathrm{Br_2} + \mathrm{O_2} + \varepsilon \quad . \quad (9)$$

$$\mathrm{C_6H_{11}Br'} + \mathrm{Br_2} \longrightarrow \mathrm{C_6H_{10}Br_2} + \mathrm{HBr} \quad . \quad . \quad (10)$$

The excited complex $\mathrm{C_6H_{12}Br_2'}$ formed in (7) can either decompose spontaneously (8), or be deactivated by collision with oxygen (9).

The rate of formation of excited bromine molecules, for weak absorption, is equal to $kI_0[\mathrm{Br_2}]$; the formation rate of the complex $= kI_0[\mathrm{Br_2}]\tau/(T + \tau)$. Since its concentration is small, its formation rate can be equated to its rate of disappearance by reactions (8) and (9) with respective velocity coefficients k_8 and k_9. The reaction rate is determined by the probability of reaction (8), which is equal to $k_8/(k_8 + k_9[\mathrm{O_2}])$. Hence the rate of bromination is given by

$$d[\mathrm{C_6H_{11}Br}]/dt = kI_0[\mathrm{Br_2}]\tau k_8/(\tau + T)(k_8 + k_9[\mathrm{O_2}])$$

There are two alternative ways in which the inhibiting effect of oxygen might operate: (*a*) In the sequence of reactions $\mathrm{Br_2} + h\nu \longrightarrow 2\mathrm{Br}$; $\mathrm{C_6H_{12}} + \mathrm{Br} \longrightarrow \mathrm{C_6H_{12}Br}$; $\mathrm{C_6H_{12}Br} + \mathrm{Br} \longrightarrow \mathrm{C_6H_{11}Br} + \mathrm{HBr}$,

the bromine atoms, in addition to combining with themselves, might be rendered inactive by the reactions $Br + O_2 \longrightarrow BrO_2$; $BrO_2 + Br \longrightarrow Br_2 + O_2$. (*b*) In the series $Br_2 + h\nu \longrightarrow Br_2'$; $C_6H_{12} + Br_2' \longrightarrow C_6H_{11}Br + HBr$, the activated bromine molecules may be deactivated by the reaction $Br_2' + O_2 \longrightarrow Br_2 + O_2$, as well as by $Br_2' \longrightarrow Br_2$. In either case, it can readily be shown that the inhibition must be dependent on the concentration of the acceptor, but since it has actually been found to be independent (see Experimental), it follows that these two hypothetical modes of operation are eliminated, and that the inhibiting mechanism is expressed by equation (9).

EXPERIMENTAL.

Pusch and Noddack in their examination of the reaction under consideration estimated the rate of removal of bromine by spectrophotometric and titration methods, but here the reaction was followed throughout its course by measuring the pressure change. Monochromatic light was employed, the green line $\lambda = 5460$ Å. from a mercury-vapour lamp and light filter being sufficiently intense to give easily measurable velocities.

The apparatus used is shown in Fig. 1. The reaction vessel used at first was a glass cylinder with flattened ends, but in the form subsequently employed the ends were of plane parallel glass fused on. It is connected by capillary tubes through two taps to reservoirs containing bromine and *cyclo*hexane. Two other connexions are made—one to the pumps, and the other to the gauge.

The pressure gauge consists of a sulphuric acid differential manometer of fine-bore tubing, connected to a mercury manometer and a large bulb kept in ice which serves to maintain a constant pressure. A two-way tap is connected to the gauge through which hydrogen and oxygen can be admitted. Exhaustion can be effected through a soda–lime tube and liquid-air trap by mercury diffusion pumps backed by an oil pump. This is necessary, as a high vacuum is required to remove oxygen and the reaction products. Connexion can also be made with a water pump when required.

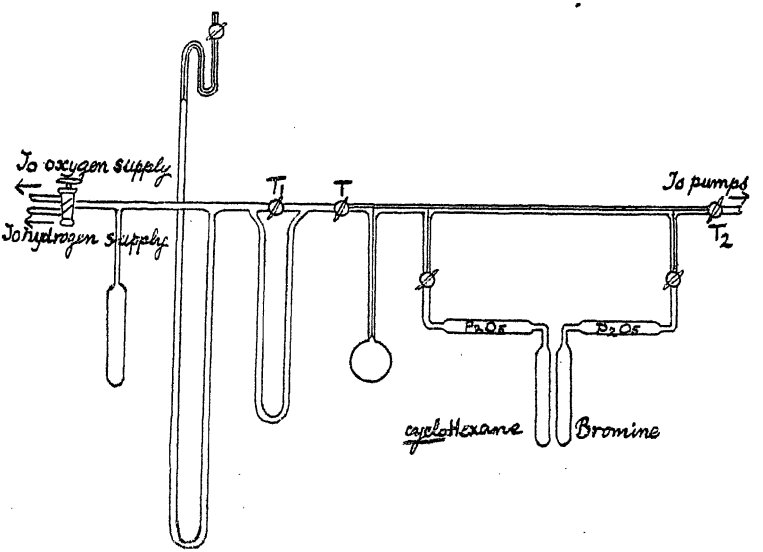
The reaction vessel is contained in a metal box, with plane parallel glass faces, through which circulates water from a thermostat constant to within $\pm 0{\cdot}1°$.

Light from the mercury lamp reaches the reaction vessel after passing through (1) a vessel with plane parallel glass faces in which cold water removes the infra-red; (2) a filter of saturated potassium dichromate solution, to which neodymium magnesium nitrate has been added until the yellow line disappears, thus isolating the

mercury green line (R. W. Wood, "Physical Optics," p. 15); and (3) an adjustable diaphragm. At first, a small glass mercury lamp was used, which was run in series with a resistance of 220 ohms from a constant 220 volts supply and took 0·65 amp. This was later replaced by a quartz mercury-vapour lamp taking 4 amps. with a *P.D.* of 150 volts, giving much more intense illumination.

Materials.—The purest obtainable bromine was further purified by distilling it twice over potassium bromide and zinc oxide, and finally over phosphorus pentoxide in an all-glass system; it was stored over phosphorus pentoxide. The *cyclo*hexane was purified

FIG. 1.



by repeated shaking with sulphuric acid, and finally by distillation. The hydrogen used in the gauge was passed over hot palladinised copper and through drying tubes. Oxygen was obtained by electrolysis of hot baryta solution and was dried before entering the apparatus.

The tap leading to the bromine reservoir was lubricated with a mixture of nujol and paraffin wax, which sufficed for some weeks without renewal. The most satisfactory lubricant for the tap to the *cyclo*hexane reservoir was a mixture of chlorinated bees' wax and aniline.

Method of Operation.—Connexion was first made between the water pump and the *cyclo*hexane and bromine reservoirs in turn, and a quantity of the vapours was drawn over to remove air present

in the reservoirs. This operation was only repeated after the taps on these reservoirs had been cleaned out.

The whole system was evacuated by the diffusion pumps for some hours. *cyclo*Hexane and bromine vapours were then admitted to the reaction vessel to known pressures, as follows: Pure hydrogen was let into the gauge up to the tap T to a measured pressure; by regulating the temperature of the *cyclo*hexane, it was then let into the system to a slight excess pressure, the tap T_1 was shut, T opened, and the excess drawn out by turning T_2 until the level on the sulphuric acid manometer was the same on both sides. T was now shut, more hydrogen was let into the gauge, and bromine vapour let into the reaction cell until the pressure was just below that in the gauge. T was then opened, T_1 shut, and bromine let in until the pressures on each side were the same.

The progress of the reaction was followed by observing the pressure decrease on the sulphuric acid manometer, T_1 being turned off when measurements were taken.

As the thermal reaction between bromine and *cyclo*hexane is appreciable at the temperatures used, it was necessary to measure this in order to ascertain the amount due to the photochemical reaction alone. This was usually done by screening off the light for a time and measuring pressure decreases due to the dark reaction only. Measurements were also made in which the thermal reaction was allowed to proceed to completion.

Before each run the system was evacuated for at least 2 hours. The reaction vessel was heated with a Bunsen burner while under a high vacuum to remove the reaction products which condensed on the cell and cut down the light entering the system.

The pressures employed (in terms of Hg, to which all measurements are reduced) were about 5 cm. of *cyclo*hexane and 4 cm. of bromine, an excess of the former being invariably present. The pressure changes finally recorded did not, in general, correspond to any definite stage in the bromine substitution, but were somewhat variable. It was therefore necessary to run the reaction to completion in each case, the final value being taken as proportional to the amount of bromine present, and bromine concentrations at any one time being deduced from the pressure changes at that time.

The following are the results of two typical runs at 30° for the dark reaction, which required about 4 hours for completion; $k = 1/t.\log_{10} a/(a-x)$. Cell A (with flattened ends) was used.

	(I.)	(II.)
Press. of bromine vapour (cm.)	3·89	3·86
,, *cyclo*hexane vapour (cm.)	5·51	5·55
Press. change for complete reaction, t_∞ (cm.)	1·620	1·470

	(I.)			(II.)		
t, mins.	Press. fall, cm.	$a - x$.	$k \times 10^4$.	Press. fall, cm.	$a - x$.	$k \times 10^4$.
0	0·606	1·014	—	0·108	1·362	—
25	0·907	0·713	64	0·509	0·961	60
50	1·088	0·532	63	0·801	0·669	62
75	1·217	0·403	57	0·961	0·509	58
100	1·320	0·300	56	1·100	0·370	55
125	1·418	0·202	55	1·198	0·272	55
150	1·480	0·140	57	1·277	0·193	57
175				1·326	0·144	59
			Mean 59			Mean 58

The thermal reaction is thus seen to conform to the unimolecular law. As the photochemical reaction also conforms to the same law, it was thought that this reaction might be due to diffuse daylight, but blackening of the lead tubes only reduced the coefficient to 0·0049, which must be due to a true dark reaction.

Temperature Coefficient of the Photochemical Reaction.—In these experiments, the first lamp mentioned on p. 2470 was used with a filter transmitting the green line. The reaction cell was filled as before, and removal of a stop let the light into the system. Readings were taken every minute, the light was shut off, and the thermal reaction velocity measured. As before, the reaction was taken to completion.

Experiments were conducted at 30° and at 40°, one of the latter being recorded as an example :

Br_2 pressure = 4·41 cm. C_6H_{12} pressure = 5·17 cm. ∞ value = 2·090 cm.

Green filter.

t.	$a - x$.	$k \times 10^4$.	t.	$a - x$.	$k \times 10^4$.	t.	$a - x$.	$k \times 10^4$.
0	1·937		8	1·598	103	12	1·451	101
5	1·718	102	9	1·556	105	13	1·417	104
6	1·682	101	10	1·522	104	14	1·385	103
7	1·635	104	11	1·484	104			Mean 103

k for thermal velocity = 70

	Press. of				
Temp.	C_6H_{12}.	Br_2.	k for green filter.	k (thermal).	k (green alone).
40°	4·41	5·17	0·0103	0·0071	0·0032
	4·03	5·27	0·0106	0·0070	0·0036
30	3·91	5·07	0·0099	0·0066	0·0033
	4·01	5·06	0·0099	0·0065	0·0034

The temperature coefficient of the photochemical reaction is thus unity within the limits of accuracy of the experiment. By the use of the mercury lamp with no filter, unimolecular coefficients were also obtained. Two experiments gave a temperature coefficient of 1·05 :

Temp.	k (total).	k (thermal).	k (photochemical alone).
40°	0·027	0·007	0·020
30	0·025	0·006	0·019

The thermal reaction appears to have only a slight temperature coefficient. In these experiments, the capillary connexions were not blackened.

The measurement of the thermal velocity coefficient at 100° gave a value of $k = 0{\cdot}011$.

The small temperature coefficient of the dark reaction would appear to point to this being a surface action rather than a true bulk reaction (compare Norrish, J., 1923, **123**, 306). Experiments with two different reaction cells at 30° gave identical velocity coefficients, and the ratio of surface area to volume was the same in each case, thus lending support to this view.

Effect of Intensity of Light.—In this series of experiments, the glass mercury lamp was replaced by a quartz lamp giving much more intense light. The reaction-cell used had plane parallel glass windows. The light intensities were compared by means of a thermopile and galvanometer. In making measurements, the thermostat cell was removed and the thermopile brought up to the same position behind the cell in each case. The intensity was varied by altering the distance of the lamp from the system, and is given in terms of the galvanometer deflexion.

Light intensity,	Pressure of		
cm.	Br_2.	C_6H_{12}.	$k \times 10^4$.
9·55	3·73	5·33	645 } Mean 654
	4·01	5·09	663 }
6·00	4·06	5·02	450
	4·02	5·07	440 } Mean 441
	3·91	5·17	435

Separate determination of the thermal velocity coefficient gave $k = 0{\cdot}0060$.

Ratio of reaction velocities = $(654 - 60)/(441 - 60) = 1{\cdot}56$.

Ratio of light intensities = $9{\cdot}55/6{\cdot}00 = 1{\cdot}59$.

The agreement shows proportionality between velocity and light intensity.

Influence of Concentration of cyclo*Hexane.*—In all the foregoing experiments, the original *cyclo*hexane pressure was within 10% of 5 cm. No general falling off of the unimolecular coefficient was observed as the *cyclo*hexane concentration was reduced during the progress of the reaction, and it would thus appear that the rate is independent of the *cyclo*hexane pressure. An attempt was made to test this point by using *cyclo*hexane pressures of from 5 to 2 cm. with 4 cm. of bromine. With 5 and 4 cm. of *cyclo*hexane, the total pressure changes for complete reaction were approximately the same, and the unimolecular coefficients were identical, corresponding to the substitution of 2—3 atoms of bromine; with 3·2 cm. the

total pressure changes were less, corresponding either to incomplete substitution or to incomplete removal of bromine. The reaction was therefore followed by direct measurement of the bromine concentration, which, together with pressure measurements, should give an indication of the extent of the substitution by bromine. This was effected by measurements of the intensity of the emergent light with a potassium photoelectric cell. The light from the mercury lamp passed through a condensing lens on to a stop placed at the focal distance from a second lens, the approximately parallel beam being passed through the reaction vessel on to the cell. The photoelectric cell was in series with a galvanometer, a high resistance, and a constant voltage of 159 volts. For calibration, galvanometer readings were taken corresponding to bromine pressures measured on the sulphuric acid manometer. The reaction could be followed by plotting galvanometer deflexions against time. Simultaneous galvanometer and pressure readings were made for experiments with various *cyclo*hexane concentrations. It was found that the bromine pressure plotted against pressure changes gave a straight line—the gradient in all cases corresponding to the substitution of two bromine atoms in the molecule—thus confirming the assumption that the bromine concentration could be taken as proportional to the difference in pressure from the infinity value. With low *cyclo*hexane concentrations, the pressure change ceased before complete removal of bromine, although, for the initial stages of the reaction, bromine pressures plotted against pressure changes gave a straight line of the same gradient as with higher *cyclo*hexane concentrations.

The table shows values of the unimolecular coefficient ($k' = 1/t.\log_{10}[Br_2]_0/[Br_2]_t$) for the removal of bromine calculated from bromine concentrations measured with the photoelectric cell for various *cyclo*hexane concentrations.

C_6H_{12} press., cm.	Br_2 press., cm.	$k' \times 10^4$.	C_6H_{12} press., cm.	Br_2 press., cm.	$k' \times 10^4$.
7·13	2·10	198	3·93	1·79	187
6·10	2·01	186	3·12	1·53	178
5·24	2·25	182	2·11	1·96	161

It will be seen that the rate is independent of the *cyclo*hexane concentration within the limits of experimental error.

Influence of Oxygen.—Preliminary experiments showed that the reaction was inhibited by oxygen. The velocity in the presence of pressures of oxygen from 0·01 to 1 cm. Hg was measured. Oxygen was let into the gauge up to the tap T to a known pressure, diluted with hydrogen, and pumped out to a measured pressure (about 2 cm. Hg); the reaction vessel was evacuated, and the oxygen–

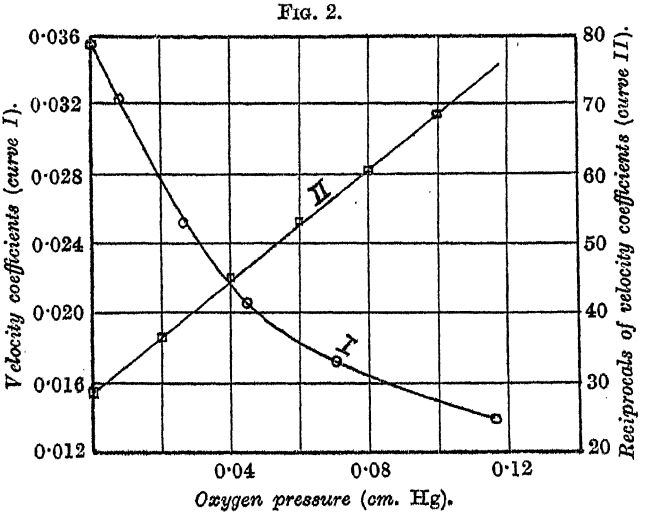
hydrogen mixture let in to the system; 5 cm. of *cyclo*hexane and 4 cm. of bromine were let into the reaction vessel as before, and the velocities measured.

In this series of experiments the capillary connexions were blackened; the thermal velocity was measured in the absence of oxygen and gave $k = 0{\cdot}0048$. The light intensity was kept constant throughout.

The table shows the velocity coefficients for various oxygen pressures. It is to be noted that the reaction still obeys the unimolecular law.

Pressures (cm. Hg) of					
O_2.	C_6H_{12}.	Br_2.	k.	k (thermal).	k (photochem.).
0·000	5·13	4·14	0·0403	0·0048	0·0355
0·0083	5·44	3·94	0·0380	,,	0·0322
0·0261	5·57	3·87	0·0300	,,	0·0252
0·045	5·05	3·96	0·0255	,,	0·0207
0·070	5·24	3·93	0·0221	,,	0·0173
0·116	5·19	3·95	0·0187	,,	0·0139
0·49	5·13	3·76	0·0094	0·0050	0·0044
1·05	4·87	4·00	0·0066	0·0045	0·0021

FIG. 2.



The thermal velocity coefficient does not diminish for oxygen pressures up to 0·49 cm., but for 1 cm. it appears to fall slightly. These results are plotted in Fig. 2 (Curve I). Curve II shows the values of oxygen pressure plotted against the reciprocals of the corresponding velocity coefficients; it will be seen that a straight line is obtained.

The inhibition by oxygen can thus be represented by the equation (compare p. 2468)

$$k_{O_2} = Kk_3/(k_3 + k_2[O_2]),$$

where K is the velocity coefficient in absence of oxygen, k_{O_2} is that for a pressure of oxygen $[O_2]$, and k_9 is a constant. From the gradient of the curve the value of k_9/k_8 is found to be 14·8, and the values deduced from the velocity coefficients with oxygen equal to 0·49 and 1·05 cm. Hg were 14·4 and 15·0, respectively, *i.e.*, agreement with this equation extends up to the highest oxygen pressures used. Experiments were not attempted at higher pressures because k_{O_2} becomes too small.

From the value of k_9/k_8, it is possible to deduce a value for the mean life of the excited complex $C_6H_{12}Br_2'$; when the oxygen pressure is expressed in mm. Hg (instead of cm.), $k_9/k_8 = 1{\cdot}48$. Now, $k_9/k_8 = (1/T)/(1/\tau)$, where τ is the mean life of the complex, and T, the time between successive collisions of oxygen and the complex (each of which is assumed to be effective in causing deactivation) for unit oxygen pressure, is given by $T = 1/A\sigma^2$, where

$$A = 2667\sqrt{2\pi N(m_1 + m_2)/R\theta m_1 m_2}$$ (Turner, *loc. cit.*).

Taking a value of σ as 10^{-7} cm. for the mean of the diameters of the oxygen molecule and the complex, we obtain $T = 2{\cdot}1 \times 10^{-8}$ sec., whence $\tau = 3 \times 10^{-8}$ sec., a value comparable with those obtained for excited molecules by other methods.

Summary and Interpretation of Results.

In the photobromination of *cyclo*hexane under conditions where the light absorption is proportional to the concentration of bromine, it is found that the photoreaction has no temperature coefficient for light of wave-length $\lambda = 5460$ Å. in the range 30—40°. The reaction rate is directly proportional to the light intensity and independent of the concentration of the *cyclo*hexane.

This form of unimolecular law is shown to be compatible, when, as in this case, no chain formation occurs, with two hypotheses: (1) the reaction may proceed through the formation of bromine atoms, or (2) the primary action may be the formation of an excited bromine molecule, the life of which is long compared with the time between collisions with a molecule of the acceptor.

The reaction velocity is reduced by the presence of oxygen. The inhibition is found to be independent of the pressure of the *cyclo*hexane. The quantitative data lead to the conclusion that not atoms but excited bromine molecules are the primary photoactive constituent; further, that it is not these excited molecules but the excited $C_6H_{12}Br_2'$ molecules which are deactivated on collision with oxygen. The mean life of this complex is *ca.* 3×10^{-8} sec. The mechanism of the photobromination and inhibition by oxygen can accordingly be described by the reactions (1A), (7), (8),

(9), and (10) (see p. 2468). The thermal bromination of *cyclo*hexane proceeds slowly on the surface of glass at 30°.

If the following values be taken for the heats (in Cals.) of linking in the various reactions employed: C–Br = 62; C–H = 87; $Br_2 \longrightarrow 2Br = 46{\cdot}2$; H + Br = HBr + 77·7; energy in the radiation $Nh\nu = 53{\cdot}2$, it is clear that the excited bromine molecule of energy content 53·2 Cals. cannot break a C–H union by impact and subsequent transference of its energy alone, but only by forming an association complex, which then undergoes rearrangement. From the above data we obtain

$$C_6H_{12} + Br_2 \longrightarrow C_6H_{11}Br + HBr + 6{\cdot}5$$
$$C_6H_{12} + Br_2' \longrightarrow C_6H_{11}Br + HBr + 59{\cdot}7$$

The products of reaction thus contain 59·7 Cals. If, as is imagined by some (Marshall, *J. Physical Chem.*, 1925, **29**, 842), the hydrogen bromide carries away this energy, there seems no reason why there should not be reaction chains in this reaction as in the bromination of toluene where similar conditions obtain. If, on the other hand, the energy is retained by the bromo-derivative, the difference in structure between bromo*cyclo*hexane and benzoyl bromide may account for the difference in reaction; in one, the transfer of energy to another bromine–hydrogen complex in the same ring is possible, forming dibromo*cyclo*hexane; in the other, the energy is localised on a side chain and can apparently only be transmitted to another molecule on collision. It is hoped to examine the chain formation in the photobromination of toluene in the near future.

Our thanks are due to Messrs. Brunner Mond for assistance in defraying part of the experimental cost, and to the Department of Scientific and Industrial Research for a grant to one of us (B. J. W.) which has enabled us to undertake this investigation.

LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE.
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CCCXXXI.—*The Preparation and Properties of* dl-*Glyceraldehyde.*

By H. GORDON REEVES.

THE importance of glyceraldehyde is twofold. Not only is it the foundation stone on which the stereochemical configuration of the carbohydrates is constructed, but also it is regarded as an important link in the elusive metabolic chain of chemical reactions by which in the animal body glucose is converted into carbon dioxide and

water. Despite this, it has received comparatively little attention owing probably to the great difficulty experienced in preparing it in a pure condition and to its lability and concomitant sensitiveness towards chemical reagents.

Nearly 70 years ago Van Deen (*Nederl. Tydschr. Geneesk.*, 1860, 4, Aug.) reported that glycerol, when treated with nitric acid or subjected to the passage of an electric current, yielded a fermentable syrup which was optically inactive. Since that time, numerous attempts have been made to prepare glyceraldehyde by the oxidation of glycerol with various agents or by electrolysis of hydroxy-acids, but in every case the yield was most unsatisfactory (for summary see Witzemann, *J. Amer. Chem. Soc.*, 1914, **36**, 1908).

In 1898, Lobry de Bruyn and Adriani (*Rec. trav. chim.*, **17**, 258) made the important discovery that by careful hydrolysis of acraldehyde dibromide, glyceraldehyde could be obtained, and in the same year Wohl (*Ber.*, **31**, 1796, 2394) synthesised the pure aldehyde from acraldehyde through glyceraldehyde diethylacetal. In 1914, Witzemann (*loc. cit.*) proved that glyceraldehyde was formed when glycerol was oxidised with Fenton's reagent (Fenton and Jackson, J., 1899, **75**, 4; *Chem. News*, 1898, **78**, 187); the syrupy product was converted into the diethylacetal by Fischer and Giebe's method (*Ber.*, 1897, **30**, 3055; 1898, **31**, 545), but only 6% of the syrup yielded an acetal, the chief impurity being dihydroxyacetone, which does not form an acetal. Owing to the presence of by-products, the glyceraldehyde, obtained by hydrolysis of the acetal with dilute sulphuric acid, could only be crystallised with great difficulty (compare Meyer and Jacobson, "Lehrbuch der Organische Chemie," I, ii, 157, 171), and the method was too tedious for practical purposes.

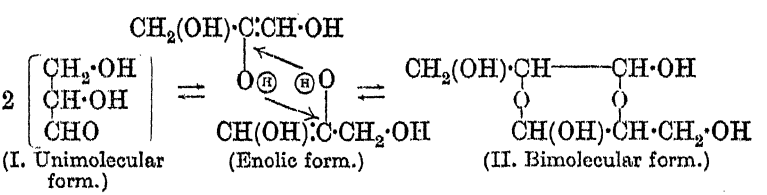
Of the many methods which have been used, that of Wohl is the only one which gives glyceraldehyde in a state of purity, entirely free from dihydroxyacetone and in reasonable yield. For this reason the material used for the present observations was prepared directly from acraldehyde (obtained by Moureu's method, *Ann. Chim.*, 1921, **15**, 158; see also Snellgrove, Thesis, London, 1924) in four stages. (1) Acraldehyde was converted into β-chloropropaldehyde diethylacetal by the action of cold absolute alcohol, saturated with dry hydrogen chloride: the yield was greatly improved by the addition of anhydrous calcium chloride. (2) The elements of hydrogen chloride were removed from the chlorinated acetal by distillation with solid potash, with production of acraldehyde diethylacetal. (3) This was oxidised by aqueous potassium permanganate to glyceraldehyde diethylacetal. (4) The last acetal was hydrolysed by means of dilute sulphuric acid, the acid neutralised, and the pure glyceraldehyde caused to crystallise from the

concentrated liquor by the addition of methyl alcohol and ether. Each of the four stages proceeds smoothly, but, although the yields have been improved in the present research, they are not good.

Glyceraldehyde, as thus obtained, is a white, non-hygroscopic, slightly sweet powder, which crystallises from aqueous methyl alcohol in colourless, pointed needles. Analysis and the m. p. of its *p*-bromophenylosazone (168°) showed it to be pure (Wohl, *loc. cit.*, gives m. p. 168°).

As a basis for the space representation of the sugars, the unimolecular formula (I) for glyceraldehyde is always adopted, but Wohl and Neuberg (*Ber.*, 1899, **32**, 1352; 1900, **33**, 3095) showed by cryoscopic determinations that it was bimolecular (compare glycollaldehyde and dihydroxyacetone) and ascribed to it the formula (II). In aqueous solution, the aldehyde gradually assumes the unimolecular form. In view of the importance of these observations, molecular-weight determinations were repeated with particular care, and the results of Wohl and Neuberg were confirmed.

In preparing the glyceraldehyde for this research, it was noted that the transparent syrup obtained by the hydrolysis of its diethylacetal had most unexpected properties. After standing over-night in a vacuum desiccator, the syrup showed a white opalescence; 24 hours later it had become very viscous and perfectly opaque. These phenomena were noted on only one occasion by Witzemann (*J. Amer. Chem. Soc.*, 1914, **36**, 2223) in his repetition of Wohl's synthesis, and his use of the term " colloidal " in this connexion was unsupported by any evidence. It seemed necessary, therefore, to investigate the molecular complexity of the aldehyde in these various states. The transparent syrup was found to be enolic and, in aqueous solution, unimolecular; the following scheme is therefore suggested as a possible mechanism for the changes described above :



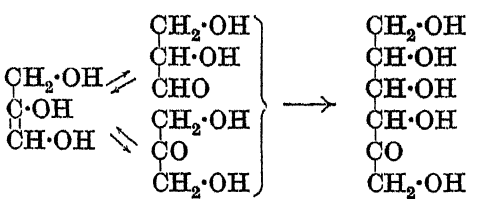
(I. Unimolecular form.) (Enolic form.) (II. Bimolecular form.)

In support of this scheme, the possibility of the formation of a stable six-atom compound from an enol, recently substantiated by Sidgwick (J., 1925, **127**, 907), may be cited. The crystalline bimolecular glyceraldehyde, after repeated crystallisation, was shown by K. H. Meyer's method (*Annalen*, 1911, **380**, 212; Meyer and Kappelmeier, *Ber.*, 1911, **44**, 2718) to contain a trace of the enol.

Fischer and Tafel (*Ber.*, 1887, **20**, 2566) showed that crude

ıymerised under the influence of dilute alkali. Wohl
ş (*loc. cit.*) found that pure glyceraldehyde in presence
ic potash solution readily condensed to β-acrose and
split up into dihydroxyacetone. Nef (*Annalen*, 1907,
910, **376**, 1; 1914, **403**, 204) showed that the first step
of dilute alkali on all carbohydrates was the production
ed enols, which then underwent decomposition by fission
le bond. Thus the γδ-dienol formed by the action of
cose breaks down at the ethylene linkage to give glycer-
The interaction of glyceraldehyde with alkali involves
e formation of a sodium salt, the metallic atom being
the carbon atom adjacent to the carbonyl group; this
onverted, by elimination of sodium hydroxide, into the
erivative, and the latter is finally converted into the

ppeared likely that in dilute alkaline solution the enolic
of glyceraldehyde could be detected by the coloration
s ferric chloride, and, actually, it was found to give a
ıtion than glucose under identical conditions.
in solutions of like concentration have the same
lex, and tables have been prepared for sugar products
. *Sugar J.*, 1907, **9**, 481), Geerligs (*ibid.*, 1908, **10**, 68),
J. Amer. Chem. Soc., 1908, **30**, 1443). It was thought
metric measurements would provide further proof of
of the enol in alkaline solution, and the results fulfilled
ıtions both for glucose and for glyceraldehyde.
ıce of the enolic modification of glyceraldehyde in
tion elucidates the mechanism of acrose formation as
Schmitz (*Ber.*, 1913, **46**, 2327). The reaction is not,
auto-condensation of glyceraldehyde, but its condens-
hydroxyacetone, which may be assumed to result from
m of the aldehyde:



lic form of glyceraldehyde was present in alkaline
been foreshadowed, since Fischer (*Ber.*, 1895, **28**, 1149)
ıt "sodium glucosate," formed by the action of sodium
glucose, had the structure

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}C(OH){:}CH{\cdot}ONa,$$

and Wohl and Neuberg (*loc. cit.*) postulated an unsaturated alcohol of the type X·C(OH):CH·OH as an intermediate phase in the conversion of glyceraldehyde into β-acrose under the influence of dilute alkali. The existence of this unsaturated labile form is now definitely proven.

The close resemblance between glyceraldehyde and glucose in chemical properties suggests the possibility of either a 1 : 2- or a 1 : 3-oxide structure rather than the generally accepted straight-chain aldehydic form.

Owing to its extreme lability, glyceraldehyde has hitherto resisted attempts to methylate it completely, but the work is being continued, and it is hoped to publish the results shortly. From the preliminary work, it would appear that glyceraldehyde falls into line with other sugars in its resistance to propylene-oxide formation.

EXPERIMENTAL.

Preparation of Glyceraldehyde.—β-Chloropropaldehyde diethylacetal. To absolute alcohol (2 mols.), cooled in an ice-bath, powdered anhydrous calcium chloride (⅛ mol.; excess should be avoided) was added, and acraldehyde (1 mol.) admitted in small portions at a time with continuous shaking. Dry hydrogen chloride (1 mol.) was now bubbled through the mixture, the temperature of the bath being kept below 5°; the mixture, which became yellow, was kept for 24 hours, during which it separated into two layers. The lower oily layer was drawn off, neutralised with finely powdered sodium bicarbonate, and dried over solid potassium hydroxide without removing the alcohol. Small quantities of the oil were recovered from the supernatant liquor by passing further quantities of hydrogen chloride. The yield was 90% of the theoretical. The pale yellow oil so obtained had a characteristic but not unpleasant odour.

Acraldehyde diethylacetal. (In this preparation exact adherence to the specified conditions is essential.) To 200 g. of the above crude oil in a 1-litre copper flask, 400 g. of pure, dry, finely powdered potassium hydroxide were added slowly in small quantities at a time with vigorous shaking and cooling. The mixture was then distilled very slowly through a three-bulb Young fractionating column; the main bulk passed over between 120° and 130°. This was dried with potassium carbonate and redistilled, the fraction distilling between 120° and 128° being collected (yield, 70%). The acraldehyde acetal was a colourless, mobile liquid with an agreeable ester-like odour, slightly soluble in water, but miscible in all proportions with alcohol and ether. It is readily hydrolysed in the cold by dilute hydrochloric acid.

Glyceraldehyde diethylacetal. The acraldehyde acetal (100 g.) was

emulsified by vigorous shaking with distilled water (1200 c.c.), and the whole cooled to 0°. To the cold emulsion was added, drop by drop with continuous and vigorous shaking, the calculated quantity of a 4% aqueous potassium permanganate solution. The mixture, after being kept for 12 hours at 0°, was heated for ½ hour on the water-bath and filtered from the precipitated manganese dioxide, which was well pressed and then twice washed with 50 c.c. of warm water. The warm filtrate and washings were treated with potassium carbonate solution (500 g. per litre) and immediately cooled; the glyceraldehyde diethylacetal, which separated as a yellow oil on the surface of the liquor, was removed, and the lower aqueous layer extracted four times with ether. The oil and the extracts were combined, and the ether was removed. The residual acetal was redistilled under diminished pressure, b. p. 130°/20 mm. A small amount of unchanged acraldehyde acetal can be recovered. The yield of glyceraldehyde diethylacetal is variable; in no case was it greater than 60%, and in one experiment it fell to 30% for no accountable reason (Wohl and Neuberg reported 40%; Witzemann, 54%). The loss here cannot be explained, since the oxidation itself proceeds quite smoothly.

The acetal is a colourless, viscous liquid with a caustic taste. It is miscible with water, alcohol, and ether, and is readily hydrolysed by dilute mineral acids. Its aqueous solution reduces Fehling's solution in the cold, and in acetic acid it gives a phenylosazone.

dl-*Glyceraldehyde.* 55 G. of the acetal were dissolved in *N*/10-sulphuric acid (550 g.) and kept at room temperature for 48 hours, then at 38° for 24 hours, and allowed to cool. The acid was exactly neutralised with the calculated weight of barium hydroxide, and the whole kept for 2 hours. The precipitated barium sulphate was filtered off and washed with a minimum volume of water. The filtrate was concentrated at 40° in a vacuum over calcium chloride. The further small amount of barium sulphate which had separated when concentration was half completed was filtered off, and concentration continued. Success in crystallisation depends on the *complete* removal of water from the syrup. After one month, a pale yellow, transparent syrup was obtained, which on standing over-night in the vacuum desiccator showed a white opalescence, and after a further 24 hours became creamy and opaque. Trituration with small amounts of pure ice-cold methyl alcohol containing 1% of ether caused immediate separation of the crystalline glyceraldehyde; yield, 60% of the theoretical. (Excess of ether must be avoided, otherwise the product is sticky.)

Properties.—The glyceraldehyde was obtained as a white, non-hygroscopic, slightly sweet powder, m. p. 133°; after being washed

with methyl alcohol, dried on porous tile, recrystallised from 40% aqueous methyl alcohol, and dried over phosphorus pentoxide in a vacuum for one week, it had m. p. 138·5° (Wohl gives 138°, and Witzemann 142°), unaltered by further recrystallisation and desiccation (Found: C, 39·8; H, 6·7. Calc.: C, 40·0; H, 6·7%). It crystallises from aqueous methyl alcohol in short, colourless needles, which are sparingly soluble in water, ethyl alcohol, and ether, and decompose above their m. p. to a sticky, brown, caramel-like mass. Its *p*-bromophenylosazone melted at 168°.

To the properties already described (Abderhalden, "Biochemisches Handlexikon," II, 1911) may be added the following: It is insoluble in benzene, petroleum, and pentane. Its solubility in water at 18° is 3 g. per 100 c.c., and it has $d_{18}^{18°}$ 1·455.

Molecular-weight Determinations.—(a) *The crystalline solid.* A freshly prepared solution containing 0·1480 g. in 25 c.c. of water gave $\Delta = 0·061°$, hence $M = 180·6$. After the solution had stood for one week, Δ was found to be 0·122°, hence $M = 90·3$. Thus dissociation into the unimolecular form occurs in aqueous solution.

(b) *The transparent syrup,* from which the crystals separated, is apparently unimolecular: 0·1204 g. in 25 c.c. of water gave $\Delta = 0·097°$; $M = 92·4$.

The Action of Alkalis and the Existence of an Enolic Modification.—Cold dilute sodium hydroxide (both $N/10$ and N) readily dissolves glyceraldehyde, which passes through all the various changes described by Nef, finally giving β-acrose, polysaccharides, and lactic acid. The alkaline solution resinifies gradually on being warmed. The aldehyde is less soluble in 50% sodium hydroxide and rapidly resinifies in the hot solution. Its behaviour with alkali is thus similar to that of other aliphatic aldehydes.

Colorimetric Measurements with Ferric Chloride Solution.—5 C.c. of 1% aqueous solutions of glucose and glyceraldehyde were each kept at 38° for 10 minutes; 5 c.c. of 0·1% caustic soda solution were then mixed with each, and the mixtures were kept at 38° for a further 10 minutes. On the addition of 1 c.c. of 10% aqueous ferric chloride, the glyceraldehyde solution showed a deeper red coloration than did the glucose solution, and therefore apparently contained a higher percentage of the enolic form. A quantitative estimation was then made with the colorimeter: 1% Aqueous solutions of glucose and glyceraldehyde were used; 2 c.c. of each were kept for 10 minutes at 38° with 7 c.c. of $N/10$-sodium hydroxide. To each was added 1 c.c. of 0·1% aqueous ferric chloride, and the solutions were cooled to room temperature.

The readings on the colorimetric scale were 1·46 and 1·15 for glucose and glyceraldehyde, respectively. Hence, the ratio of enol

in glyceraldehyde to that in glucose = 1·27 : 1. Similar results were obtained with several different preparations.

Refractometric Measurements.—Readings were taken with a Pulfrich refractometer at 20° with sodium light. The following solutions were prepared:

(*a*) *Neutral solution.* 2 C.c. of 1% glucose solution were warmed at 38° for 5 minutes with a mixture of 2 c.c. of *N*/10-hydrochloric acid and 2 c.c. of *N*/10-sodium hydroxide, and cooled to room temperature.

(*b*) *Acid treatment.* As in (*a*), but the alkali was not added until after the cooling.

(*c*) *Alkali treatment.* As in (*a*), but the acid was omitted until after the cooling.

(*d*) A 1% aqueous solution of glucose, as a standard.

Solutions similar to (*a*), (*b*), (*c*), and (*d*) were prepared with glyceraldehyde. The readings obtained show that there is a decrease of 2′ in the angle of refraction of both glucose and glyceraldehyde in alkaline solution, indicating the production of an unsaturated form. These results were confirmed on several occasions with different preparations.

Nature of solution.	Glucose.	Glyceraldehyde.
(*d*) Aqueous (1%)	67° 2′	67° 2′
(*a*) Neutral (⅓%)	67° 9′	67° 8′
(*b*) Acid (⅓%)	67° 9′	67° 8′
(*c*) Alkaline (⅓%)	67° 7′	67° 6′

There is no change in the refractive index of the glyceraldehyde solution after standing for one month.

From (*d*) the refractive index for a 1% solution = 1·33412, whereas that for water is 1·33311 under the same conditions. Hence $[R_L]_D = 19·2$ (calc. for $C_3H_6O_3$: 19·14; for enolic form: 20·08), showing that in aqueous solution no appreciable amount of the enolic form exists, a fact which is substantiated in that ferric chloride gives no coloration.

Bromine Titration for Estimation of the Enol.—A suspension of glyceraldehyde in chloroform slowly decolorises a cold solution of bromine in the same solvent. An alcoholic solution of glyceraldehyde rapidly decolorises alcoholic bromine at −7°.

The bromine titration was carried out as follows: A solution of 0·1 g. of glyceraldehyde in 250 c.c. of absolute alcohol was cooled in ice and salt for ½ hour. Ice-cold *N*/10-alcoholic bromine solution was run in slowly from a burette until the yellow colour of the bromine just persisted (10—12 c.c. usually); 2—3 c.c. of a 10% alcoholic solution of β-naphthol, freshly prepared, were added to

remove the excess of bromine, followed by 15 c.c. of 10% potassium iodide solution, and the mixture was boiled on the water-bath for 10 minutes. The resulting pale yellow solution was cooled and titrated against $N/100$-sodium thiosulphate (usually 1—2 c.c.). The average of four experiments gave enol = 0·54%.

An alcoholic solution of the syrup from which the solid glyceraldehyde was obtained readily decolorised alcoholic bromine solution. Bromine titrations on this syrup (0·1 g. in 50 c.c. of absolute alcohol) gave 5·7% of enol (mean of four experiments).

These results show that, although the crystalline form of glyceraldehyde is contaminated with a little enol, the syrup from which the crystals are obtained contains ten times as much.

The author expresses his thanks to the Royal Society for a grant which has partly defrayed the cost, also to Dr. R. H. Pickard, F.R.S., in whose laboratory the acraldehyde was prepared, to Professor W. N. Haworth for his interest, and to Dr. J. A. Hewitt for suggesting the work and for advice throughout its progress.

KING'S COLLEGE, W.C. 2. [*Received, August 13th*, 1927.]

CCCXXXII.—*Examples of Feeble Activation of Certain Extended Conjugated Systems by Doubly Bound Oxygen.*

By ROBERT ROBINSON and AHMAD ZAKI.

ALTHOUGH it has recently been shown (Moore and Tucker, *J. Amer. Chem. Soc.*, 1927, **49**, 258) that one of the products of the sulphonation of cinnamic acid is the *m*-derivative, there is a mass of evidence demonstrating the *op*-orienting influence of ethenoid and benzenoid groups. It is therefore surprising to find this contested by Baker and Wilson (this vol., p. 843), especially on the basis of the facts summarised in the scheme below dealing with the results of nitration experiments.

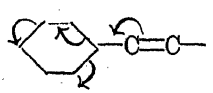
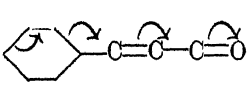
$Ph\cdot CH{:}CH\cdot NO_2$ (meta, 2%)	$Ph\cdot CH_2\cdot CH_2\cdot NO_2$ (meta, 13%)
$Ph\cdot C(NO_2){:}CH\cdot C_6H_4\cdot NO_2$ (meta, 21%)	$Ph\cdot CH_2\cdot NO_2$ (meta, 50%)

The first three cases are quoted by Baker and Wilson, and instead of phenylnitromethane they mention its dimethyl derivative, $Ph\cdot CMe_2\cdot NO_2$ (meta, 29%). This comparison is not just, because the electron displacement due to the methyl groups must, in accordance with the theory of Allan, Oxford, Robinson, and Smith (J.,

1926, 401) (adopted by Baker and Wilson), have an *op*-orienting effect. Again the nitroxyl group in the *p*-nitrobenzylidenephenylnitromethane should have a weak *m*-directive influence. The disparity, 21—29, in itself indicates the *op*-influence of the unsaturated group, whilst the disparity 21—50 demonstrates it. The argument may be stated as follows. The substitution of nitroxyl for hydrogen in toluene and in the corresponding position in nitrostilbene produces a much smaller change in the direction of *m*-orientation in the latter case. Therefore the *op*-directive power of $\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$ is greater than that of $\cdot CH_3$. Thus the actual evidence put forward by Baker and Wilson leads to a conclusion diametrically opposed to that which they draw.

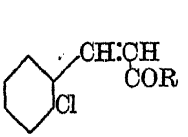
The view advanced by Baker and Wilson is that the effect of the positive change of the nitro-group in ω-nitrostyrene may conceivably be neutralised in the adjustable electric field of the unsaturated centre. Unless the whole unsaturated group has a real net negative charge, this does not appeal as sound electrostatics; and if it has a negative charge, as the result of interaction with the surroundings, then *ipso facto* it would be *op*-directive. The *op*-directive effect of unsaturated groups may be deduced, not only from such widespread phenomena as the *op*-substitution of diphenyl and derivatives, but also indirectly from the increased reactivity of conjugated unsaturated substances in certain directions and especially towards kationoid reagents (compare, for example, K. Meyer and Schoeller, *Ber.*, 1919, **52**, 1468, on the preparation of an azo-derivative of dimethylbutadiene). An interesting example of *op*-direction by an unsaturated group was encountered a few years ago by Miss Margaret D. Scott Murray (University of St. Andrews), who nitrated ethyl benzylidenecyanoacetate in sulphuric acid solution at − 5° to − 10° by means of potassium nitrate (5 mols.). The *o*- and *p*-nitro-derivatives were alone isolated, although not in good yield, and identified by comparison with authentic specimens.

Our view of the cause of the *op*-substitution of cinnamic acid and similar substances is that it is due to the butadienoid-type conjugation of the unsaturated centre with the nucleus as shown in the expression (I).

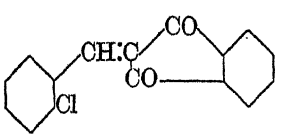
(I.)   (II.)

The crotonoid, conjugated polarisation shown in (II) will doubtless exist in certain phases of the molecule, but should not lead to *m*-substitution, because in these phases the reaction velocity is

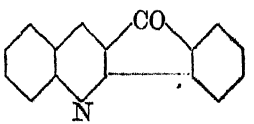
greatly diminished as the result of the positive field over the nucleus, the reagent being kationoid. If the conjugated polarisation were permanent and pronounced, the condition (I) might never be realised, but there is reason to believe that the degree of activation and coherence of all such systems is small. An excellent example is that of *m*-nitrotoluene, in the further nitration of which the methyl group is able to take complete control (Vorländer has shown that the same conditions obtain in quaternary salts derived from *m*-toluidine). Here the methyl group initiates a process favouring reaction, whilst the effect of the nitroxyl is to diminish the reaction velocity, and although the charges associated with the nitroxyl are generally supposed to be much greater than those appearing as the result of the small electron displacement caused by the methyl group, yet it is obvious that phases must occur in which the latter can be effective. The positive field due to the nitroxyl is thus considered to undergo variations; whilst it is considerable over the nucleus, nothing happens, but when, probably as the result of the approach of other charges, the shadow lifts, the molecule becomes, momentarily, equivalent to one of toluene, and substitution in the *o*- and *p*-positions with respect to the methyl group occurs rapidly. An analogous conception applies to systems like those of phenylnitromethane (with two obvious modifications), ω-nitrostyrene and cinnamic acid. The weak coherence of the unsaturated units (C=C, C=O, N=O, C≡N, etc.) in the crotonoid and semi-crotonoid systems is obviously better demonstrated by the occasional failure to exhibit their characteristic properties than by the absence of an anticipated inhibitory effect as in the examples discussed above. We suspect that activation of a mixed system comprising the characteristic group (CO, NO_2, etc.), an aromatic unsaturated group including an even number of carbon atoms, and an ethenoid group is always feeble and have investigated this in three directions. The behaviour of the chlorine atom of *o*- and *p*-nitrochlorobenzene, which is replaceable by anions, is simulated by that of *o*-chlorobenzaldehyde and *o*-chlorobenzoic acid. We have tested the degree of reactivity



(III.)



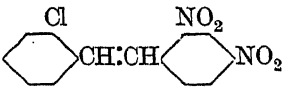
(IV.)

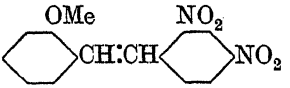


(V.)

of the chlorine atom in the system (III) by attempting a condensation with ammonia which might give a quinoline derivative.

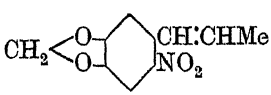
This is a stringent test, in view of the facility with which the quinoline ring may be constructed, but it gave entirely negative results under varied conditions with *o*-chlorobenzylideneacetophenone and ethyl *o*-chlorobenzylidenecyanoacetate. In the case of *o*-chlorobenzylidenediketohydrindene (IV), a greater reactivity would be expected owing to the existence of the two carbonyl groups and it was indeed found possible to convert the substance into the ketoindenoquinoline (V), although in very small yield.

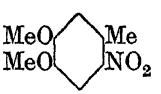
(VI.) 



(VII.)

Similar inactivity has been noted in the stilbene derivatives (VI) and (VII); the former does not react with *p*-toluidine as 2 : 4-dinitrochlorobenzene does, and the latter, unlike 2 : 4-dinitroanisole, is resistant to hydrolytic agents. The inactivity of 1 : 5-dinitronaphthalene, of 2 : 2′-dinitrodiphenyl, and of 2 : 2′-dichloro-6 : 6′-dinitro-4 : 4′-ditolyl towards methyl-alcoholic ammonia at 150° (Burton and Kenner, J., 1922, **121**, 495) also exemplifies the phenomenon of limited conjugation. Finally, 6-nitro*iso*safrole (VIII) has been prepared and we find that the methyl group in it is relatively inert, because an anhydrocotarninenitro*iso*safrole could not be obtained, although 6-nitrohomoveratrole (IX) is readily converted into anhydrocotarninenitrohomoveratrole (Robinson and Robinson, J., 1914, **105**, 1456).

(VIII.) 



(IX.)

In this case, the dissociating semi-crotonoid system, which the molecule formally contains, does not function.

EXPERIMENTAL.

Phenyl 2-chlorostyryl ketone did not yield a quinoline derivative and was recovered unchanged after heating with alcoholic urea and copper powder at 200°, or after boiling with aniline and copper powder. Ethyl 2-chloro-α-cyanocinnamate behaved similarly.

2-*o*-*Chlorobenzylidene*-1 : 3-*diketohydrindene* (IV).—*o*-Chlorobenzaldehyde and diketohydrindene in molecular proportion were heated together at 120°; the product, obtained in excellent yield, crystallised from alcohol in yellow, prismatic needles, m. p. 130—131° (Found: C, 71·3; H, 3·4. $C_{16}H_9O_2Cl$ requires C, 71·5; H, 3·3%). This diketone (2·9 g.), mixed with urea (1 g.), 95% alcohol (5 c.c.), copper powder (0·25 g.), and a trace of cupric chloride, was heated in a sealed tube at 240—250° for 14 hours. On working

up the products from three such experiments, 100 mg. of a weak, yellow base, crystallising from alcohol, were obtained. The substance had m. p. 172—173°, and mixed with ketoindenoquinoline (m. p. 176°; Noelting and Blum, *Ber.*, 1901, **34**, 2470) it melted at 174—175°. The substance could not be obtained at all in experiments made under less drastic conditions and the degree of lability of the halogen in the chlorobenzylideneindandione is evidently negligible.

2′-*Chloro*-2 : 4-*dinitrostilbene* (VI).—A mixture of 2 : 4-dinitrotoluene (52 g.), *o*-chlorobenzaldehyde (40 g.), and piperidine (5 c.c.) was heated on the steam-bath until it set to a solid mass. The product was broken up and boiled with alcohol, the mixture cooled, and the solid isolated. The substance crystallised from alcohol in slender, lemon-yellow needles or from ethyl acetate in bright yellow, prismatic needles, m. p. 174°, that reflect light of many colours (Found: N, 9·4. $C_{14}H_9O_4N_2Cl$ requires N, 9·2%). This stilbene derivative is sparingly soluble in most organic solvents and is most easily crystallised in quantity from acetic acid or by the addition of alcohol to a solution in nitrobenzene. The reactivity of the chlorine atom could not be demonstrated, the substance being recovered unchanged after prolonged boiling with alcoholic *p*-toluidine or after heating with alcoholic ammonia at 100° for several hours. Its hot solution in piperidine is brownish-yellow and becomes green on cooling; if alcohol is added to the hot solution, a copious separation of unchanged material occurs.

2 : 4-*Dinitro*-2′-*methoxystilbene* (VII).—The preparation was like that just described and the product crystallised from acetone in reddish-orange, stout, prismatic needles, m. p. 176° (Found: N, 9·5. $C_{15}H_{12}O_5N_2$ requires N, 9·3%). This substance is more sparingly soluble in most solvents than the chlorodinitrostilbene; its solutions are yellow and deposit orange needles on cooling. All attempts to replace the methoxy-group by NH_2, NHR, or NR_2, and also to hydrolyse the substance by boiling aqueous and aqueous-alcoholic alkalis, were fruitless.

6-*Nitro*iso*safrole* (VIII).—Bromodihydrosafrole, b. p. 160°/16 mm., is a heavy, almost colourless oil which was obtained by the action of hydrobromic acid (saturated at 0°) on an equal weight of safrole. On heating with aniline, it yields *iso*safrole unmixed with safrole. Since *iso*safrole could not be directly nitrated, the safrole hydrobromide was nitrated and nitro*iso*safrole obtained from the product. Bromodihydrosafrole (20 g.) dissolved in acetic acid (120 c.c.) was nitrated by the gradual addition, with cooling, of a mixture of nitric acid (30 c.c.; *d* 1·42) and acetic acid (30 c.c.). The product was isolated by means of ether after 20 minutes and boiled for

5 minutes with alcohol (100 c.c.) containing potassium hydroxide (10 g.). The solid then precipitated by water crystallised from aqueous methyl alcohol in lemon-yellow needles, m. p. 88° (Found: C, 58·2; H, 4·4; N, 7·0. $C_{10}H_9O_4N$ requires C, 58·0; H, 4·3; N, 6·8%). The substance is readily soluble in most organic solvents, giving yellow solutions, and in sulphuric acid, from the bright red solution in which it is not recovered unchanged. It yields 6-nitropiperonal, recognised by the preparation of its phenylhydrazone, on oxidation with sodium dichromate and hot dilute sulphuric acid. Experiments on the condensation of this substance with ethyl oxalate in presence of alcoholic potassium ethoxide gave ambiguous results; no definite product was isolated. On the other hand, condensation with cotarnine in ethyl-alcoholic solution containing sodium ethoxide did not occur at all.

6-*Amino*iso*safrole*.—Nitro*iso*safrole (6 g.) mixed with tin (15 g.) and concentrated hydrochloric acid (35 c.c.) was heated on the steam-bath until reduction was complete. The amine was extracted by ether and isolated as its very sparingly soluble hydrochloride. The regenerated base crystallised from light petroleum in colourless needles, m. p. 68—69° (Found: C, 67·5; H, 6·2. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2%). It is readily soluble in organic solvents, and may be diazotised and thereafter coupled with β-naphthol to give a crimson azo-derivative. The *hydrochloride* separates from hot water in colourless needles. *Acetamido*iso*safrole* crystallises from alcohol in slender, colourless needles, m. p. 206°, and yields an oily dibromide which is converted into 5 : 6-methylenedioxy-2-methylindole by treatment with alcoholic potassium hydroxide (compare Foulds and Robinson, J., 1914, **105**, 1967).

THE UNIVERSITY, MANCHESTER. [*Received, July 18th*, 1927.]

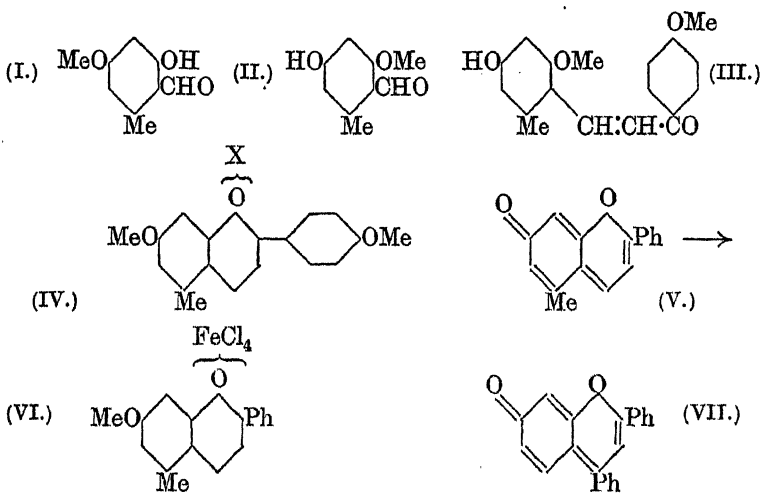
CCCXXXIII.—*Derivatives of Orcinol. Part I.*

By EDMUND LANGLEY HIRST.

IT has become apparent, during investigations which are now in progress into the structure of certain members of the group of lichen acids, that special importance must be attached to the isomeric orcylaldehyde monomethyl ethers as intermediate substances in synthetic work. It was therefore deemed advisable as a preliminary step to obtain further and more definite chemical evidence concerning the orientation of these two isomerides. This was effected by studying the condensation products of the two methylated aldehydes with acetophenone and with simple sub-

stituted derivatives of acetophenone. Under the appropriate conditions, orcylaldehyde 5-methyl ether (I) would be expected to yield pyrylium salts directly, in the same manner as does resorcylaldehyde (compare Perkin and Robinson, P., 1907, **19**, 149; Decker and von Fellenberg, *Ber.*, 1907, **40**, 3815), whereas the isomeric 3-methyl ether (II) could not do so. When the experiment was made, the orcylaldehyde monomethyl ether (m. p. 188°) described by Gattermann (*Annalen*, 1907, **357**, 346) failed to yield a pyrylium salt either with acetophenone or with acetylanisole, whilst with the latter reagent in the presence of alkali it gave the unsaturated *ketone* (III), which did not give a pyrylium salt until demethylation had been effected by means of hydriodic acid.

The orientation of the original substance as orcylaldehyde 3-methyl ether (4-hydroxy-2-methoxy-6-methylbenzaldehyde), which was previously proposed by Gattermann, is thus confirmed. On the other hand, the isomeric orcylaldehyde monomethyl ether (everninaldehyde; Hoesch, *Ber.*, 1913, **46**, 886) readily formed pyrylium salts when condensed with acetophenone in an acid medium and it must accordingly be orcylaldehyde 5-methyl ether (I).



Amongst the compounds investigated, the 4′ : 7-dimethoxy-2-phenyl-5-methylbenzopyrylium salts (IV) obtained from everninaldehyde and acetylanisole were remarkable for their exceedingly intense powers of fluorescence; qualitative comparisons of pyrylium salts from the two orcylaldehyde monomethyl ethers and from orcylaldehyde indicated that the greatly enhanced fluorescent activity of the 4′ : 7-dimethoxy-compounds is connected with the simultaneous presence of the two methoxy-groups in the molecule.

The properties and behaviour of all the compounds examined were strictly normal and comparable with those of pyrylium salts prepared from resorcylaldehyde or similar substances. Details will be found in the experimental section.

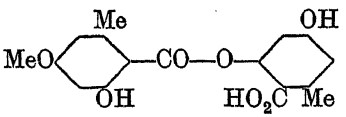
Attempts to prepare the bases corresponding to these pyrylium salts led in each case to the isolation of the anhydro-base. Very few of these compounds have hitherto been examined in detail on account of the difficulty experienced in obtaining them in a crystalline condition, and in the present work only one anhydro-base has been made to crystallise : *7-hydroxy-2-phenyl-5-methylbenzopyrylium chloride* gave with sodium acetate a red *base* (V) which could be crystallised (although with difficulty) from its solution in benzene. A study of its properties showed that it was a normal example of a base of the anhydronium type. Thus it formed, when heated with methyl sulphate, a salt of *7-methoxy-2-phenyl-5-methylbenzopyrylium hydroxide*, which was identified by direct comparison of the corresponding *ferrichloride* (VI) with an authentic specimen. A similar transformation of the anhydro-base by reaction with methyl iodide could not be effected, the failure being due in all probability to the insoluble nature of the base. The reaction with methyl sulphate renders the base directly comparable with the compound (VII) which was isolated in a crystalline condition by Armit and Robinson (J., 1925, **127**, 1604), and the discovery of this further example provides additional experimental evidence in support of the views of these authors regarding the structure of anhydronium bases.

Further evidence in support of the constitutional formulæ assigned to the orcylaldehyde monomethyl ethers has been obtained by connecting the present series of experiments with the work of Fischer and Hoesch (*Annalen*, 1912, **391**, 347) on the partly methylated orsellinic acids. This was accomplished by preparing from orcylaldehyde 3-methyl ether the corresponding carbomethoxy-derivative, *5-methylcarbonato-orcylaldehyde 3-methyl ether* (*5-methylcarbonato-3-methoxy-o-tolualdehyde*). This substance was oxidised in neutral solution by potassium permanganate to give 5-methylcarbonato-3-methoxy-o-toluic acid (5-methylcarbonato-orsellinic acid 3-methyl ether), which had been prepared directly from orsellinic acid by Fischer and Hoesch (*loc. cit.*).

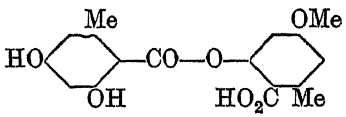
5-Methylcarbonato-orcylaldehyde 3-methyl ether is a phototropic substance, turning deep yellow when exposed to light for a few hours and becoming colourless again in the dark.

The action of alkali on 5-methylcarbonato-orsellinic acid 3-methyl ether led to the formation of orsellinic acid 3-methyl ether. The alternative formulæ suggested by Perkin and Everest (" The

Natural Organic Colouring Matters," 1918, pp. 549 and 551) for ramalic acid (one of the commoner lichen acids) require, in the form in which they are printed, that orsellinic acid 3-methyl ether should be one of the products formed on hydrolysis. But it was found by Hesse (*J. pr. Chem.*, 1898, **57**, 253; compare Perkin and Everest, *op. cit.*) that everninic acid and not orsellinic acid 3-methyl ether is obtained when ramalic acid is hydrolysed. In view of Fischer's work on evernic acid (*Ber.*, 1913, **46**, 3253; 1914, **47**, 505), which fixes its structure by relating it to lecanoric acid (Fischer and Fischer, *Ber.*, 1913, **46**, 1138), the alternative formulæ possible for ramalic acid should therefore be (VIII) and (IX). Experiments are now in progress by means of which it is hoped to be able to make a decision between the two.



(VIII.)



(IX.)

EXPERIMENTAL.

Pyrylium Salts from Orcylaldehyde.—(a) Orcylaldehyde (2 g.; prepared from orcinol by Gattermann's method, *loc. cit.*) and acetophenone (2 g.) were condensed in methyl-alcoholic solution (10 c.c.) by saturating the cold mixture with dry hydrogen chloride. The crystalline precipitate that appeared after a few minutes (yield, almost quantitative) was washed with a little methyl alcohol and recrystallised from hot water containing a little hydrochloric acid, *7-hydroxy-2-phenyl-5-methylbenzopyrylium chloride* being obtained in long, yellow needles, m. p. 206° (decomp.) after darkening at 170°. The *perchlorate* (orange, rectangular prisms, m. p. indefinite but below 245°), *iodide* (red, rectangular prisms, m. p. 225° decomp.), *mercurichloride* (golden needles, m. p. 229—230° decomp.), and *ferrichloride* (golden-brown needles, m. p. 147—148° decomp. Found: C, 44·0; H, 3·3. $C_{16}H_{13}O_2Cl_4Fe$ requires C, 44·1; H, 3·0%) were prepared from the chloride by the usual methods. The behaviour of all the salts was normal. The chloride showed no fluorescence in methyl alcohol, but gave an apple-green fluorescence with sulphuric acid.

The corresponding *anhydro-base* (V) was precipitated by sodium acetate from a hot solution of the chloride in water. It was obtained crystalline on very slow evaporation of its solution in benzene, as dark red needles, which sintered and melted with decomp. at 156—165° (Found: C, 81·4; H, 5·5. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%). The base was very slightly soluble in water and showed

a slight fluorescence in methyl alcohol. Boiling hydrochloric acid regenerated the chloride (m. p. 206°). The dry base did not react with methyl iodide in boiling benzene. When, however, the base was heated for 2 hours at 120° with an excess of freshly distilled methyl sulphate, reaction ensued and on addition of a mixture of hot water and hydrochloric acid, saturated with ferric chloride, *7-methoxy-2-phenyl-5-methylbenzopyrylium ferrichloride* was precipitated. This crystallised from acetic acid in golden-yellow, rectangular plates or needles, m. p. 181° (decomp.), and was identified by direct comparison with an authentic specimen (see below) (Found: C, 45·5; H, 3·6. $C_{17}H_{15}O_2Cl_4Fe$ requires C, 45·4; H, 3·3%).

(b) Orcylaldehyde and acetylanisole gave in good yield, under conditions similar to the above, *7-hydroxy-4'-methoxy-2-phenyl-5-methylbenzopyrylium chloride*. This was insoluble in dilute hydrochloric acid and crystallised from methyl alcohol–dilute hydrochloric acid in red needles, m. p. 242—243° (decomp.) after darkening at 225° (Found: C, 61·6; H, 5·7. $C_{17}H_{15}O_3Cl,1\frac{1}{2}H_2O$ requires C, 61·9; H, 5·5%). The *iodide* (microscopic, red prisms, m. p. 235—236° decomp.) was insoluble in all the solvents tried, whereas the *ferrichloride* (yellow needles or elongated plates, m. p. 149—150° decomp.) was much more readily soluble in acetic acid than the corresponding 7-hydroxy-2-phenyl-5-methylbenzopyrylium ferrichloride. The chloride fluoresced strongly in sulphuric acid and in methyl alcohol and weakly in water and in acetic acid.

Pyrylium Salts from Everninaldehyde (Orcylaldehyde 5-Methyl Ether).—Hoesch's orcylaldehyde monomethyl ether (everninaldehyde, *Ber.*, 1913, **46**, 886) (2 g.) was dissolved in methyl alcohol (10 c.c.) containing acetophenone (2 g.), and dry hydrogen chloride was passed into the cooled solution. A brown, crystalline precipitate (2·5 g.) separated after a few minutes. This was filtered off, washed with cold methyl alcohol, and recrystallised from hot dilute hydrochloric acid, thus giving needles, m. p. 173—174° (decomp.), of *7-methoxy-2-phenyl-5-methylbenzopyrylium chloride* containing $1\frac{1}{2}$ molecules of water of crystallisation (Found: C, 65·3; H, 6·05. $C_{17}H_{15}O_2Cl,1\frac{1}{2}H_2O$ requires C, 65·1; H, 5·8%). The *iodide* (red, microscopic needles, m. p. 191—192° decomp.) and the ferrichloride (needles or rectangular plates from acetic acid; m. p. 181—182° decomp., after softening at 177°) were prepared in the usual way from the chloride. All the salts gave an intense apple-green fluorescence in water, methyl alcohol, or sulphuric acid.

Everninaldehyde, when condensed in a similar manner with acetylanisole, gave *4': 7-dimethoxy-2-phenyl-5-methylbenzopyrylium chloride*, which crystallised from dilute hydrochloric acid in light

red needles, m. p. 214—215° (decomp.) (Found: C, 62·9; H, 5·9. $C_{18}H_{17}O_3Cl,1\frac{1}{2}H_2O$ requires C, 62·8; H, 5·8%). The *ferrichloride* crystallised from acetic acid in yellow needles, m. p. 177° (decomp.). The chloride and the ferrichloride gave a very intense apple-green fluorescence in all solvents.

Condensation of Orcylaldehyde 3-Methyl Ether with Acetylanisole.—When Gattermann's orcylaldehyde 3-methyl ether (m. p. 188°) (2 g.), acetylanisole (1·9 g.), and potassium hydroxide (2 g. in 3 c.c. of water) were heated on the water-bath for 3½ hours in methyl-alcoholic solution (20 c.c.), condensation occurred to give p-*anisyl 4-hydroxy-2-methoxy-6-methylstyryl ketone* (III). Addition of water then gave an oil (decomposition products) and from the decanted liquor, on cooling, crystals of the ketone separated in yellow needles, m. p. 194—195° (Found: C, 64·8; H, 6·5. $C_{18}H_{18}O_4,2H_2O$ requires C, 64·7; H, 6·6%). The action of hydriodic acid on this substance led to demethylation followed by condensation to a pyrylium salt which showed an intense green fluorescence in concentrated sulphuric acid.

5-*Methylcarbonato-orcylaldehyde 3-Methyl Ether*.—Orcylaldehyde 3-methyl ether (5 g.) was dissolved in 50 c.c. of acetone and treated with methyl chloroformate (4 c.c.). The solution was cooled in ice and shaken vigorously during the addition of 60 c.c. of *N*-sodium hydroxide. An oil separated which was washed several times with cold water and soon solidified. This material crystallised from dilute acetone in long, colourless, phototropic needles, m. p. 80—81° (Found: C, 58·8; H, 5·2. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%).

5-Methylcarbonato-orcylaldehyde 3-methyl ether (5 g.) dissolved in acetone (25 c.c.) was treated gradually with a solution of potassium permanganate (6 g. in 100 c.c. of water containing 5 g. of crystallised magnesium sulphate), the temperature being maintained at 45°. The precipitated oxides of manganese were then removed by means of sulphur dioxide in the usual way. A quantity of oil separated from the clear solution, followed by a slow crystallisation of 5-methyl-carbonato-orsellinic acid 3-methyl ether. Recrystallisation from ligroin–ethyl acetate gave the pure compound in colourless needles, m. p. 144° (yield, 2 g.). This substance yielded orsellinic acid 3-methyl ether when hydrolysed by Fischer and Hoesch's method (*loc. cit.*).

UNIVERSITIES OF MANCHESTER AND BIRMINGHAM.

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CCCXXXIV.—*The Nature of the Supposed Dimethiodide of Trimethylene Sulphide.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

IN reviewing the organic compounds of nitrogen and sulphur from the point of view of the octet theory, Langmuir (*J. Amer. Chem. Soc.*, 1920, **42**, 274) mentioned the dimethiodide of trimethylene sulphide (Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880) as the only substance known of the type $[SR_4]I_2$, the sulphur atom forming the centre of a positive bivalent ion. Although this compound can be satisfactorily formulated in accordance with the electronic theory of valency, no reason was apparent why this (together with the corresponding derivative of 2-methyltetramethylene sulphide) should have been the only dimethiodide of a sulphide to be isolated. We thought it desirable, therefore, to examine the substance in greater detail and to prepare other salts derived from this novel type of ion.

In the course of these experiments, we have found that the substance does not possess the structure $\left[CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>S<\begin{matrix}Me\\Me\end{matrix}\right]I_2$ attributed to it. It was stated explicitly by Grischkevitsch-Trochimovski that the two atoms of iodine in the molecule of the compound are equally ionic, but we were led to doubt this by the observation that only half the iodine is immediately precipitated by silver nitrate in cold aqueous solution, the rest being thrown down when the solution is boiled. This indicates the presence in the molecule of one atom of iodine in the ionic condition and a second atom highly reactive but not actually ionised. In agreement with this view, a solution of the supposed dimethiodide, after being shaken with an excess of silver chloride, yielded a *chloroplatinate*, $[CH_2I{\cdot}CH_2{\cdot}CH_2{\cdot}SMe_2]_2PtCl_6$, and a *chloroaurate*,

$$[CH_2I{\cdot}CH_2{\cdot}CH_2{\cdot}SMe_2]AuCl_4,$$

each with iodine still present in the molecule.

The compound produced by the addition of methyl iodide to trimethylene sulphide is therefore dimethyl-γ-iodopropylsulphonium iodide. Its formation is readily interpreted as due to reversible sulphonium salt formation (compare Bell, Bennett, and Hock, this vol., p. 1803). The strain in the four-membered ring will cause the monomethiodide, which must presumably be first formed, to pass over by intramolecular dissociation into methyl γ-iodopropyl sulphide, which will then combine with a second molecular proportion of methyl iodide:

$$C_3H_6S + MeI \longrightarrow \left[CH_2\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle SMe\right]I \longrightarrow CH_2I\cdot CH_2\cdot CH_2\cdot SMe \longrightarrow [C_3H_6I\cdot SMe_2]I.$$

Independent confirmation of the structure of the compound in question has also been obtained by synthesis. Methyl γ-hydroxypropyl sulphide, prepared by methylating γ-hydroxypropyl mercaptan (Rojahn and Lemme, *Arch. Pharm.*, 1925, **263**, 612), yielded an oily methiodide which reacted rapidly with hydrogen iodide to yield dimethyl-γ-iodopropylsulphonium iodide, identical with the supposed dimethiodide of trimethylene sulphide.

It follows also that the " dimethiodide " of 2-methyltrimethylene sulphide is either dimethyl-γ-iodo-α-methylpropylsulphonium iodide or dimethyl-γ-iodo-*n*-butylsulphonium iodide.

There is thus no reason to believe that a dimethiodide of a sulphide can exist. Although the electronic formula of such a substance would be analogous to that of a sulphone, $R_2\overset{+}{\underset{+}{S}}\langle\begin{matrix}\bar{O}\\\bar{O}\end{matrix}$, the relative difficulty of formation of the former is easily understood. The conversion of a methiodide into a dimethiodide would be opposed by a large force, since it would involve the addition of a second equal charge to a sulphur atom already bearing a full free positive charge. This force must prevent the formation of a dimethiodide of a monosulphide, for similar forces make the addition of a second molecule of methyl iodide difficult or impossible even in the case of such substances as 1 : 4-dithian and pyrazine, where there are present in the molecule two distinct atoms of sulphur or nitrogen at which addition might occur. The relative ease with which a sulphoxide is converted into a sulphone, on the other hand, results from the diminution in these compounds of the field due to each positive charge by the influence of the free negative charge on the adjacent oxygen atom.

Experimental.

Preparation of Trimethylene Sulphide.—An improved yield of trimethylene sulphide was obtained thus : A solution of sodium sulphide (80 g. of the hydrate) in water (80 c.c.) and alcohol (100 c.c.) was divided into unequal portions, one-third being boiled in a flask under reflux whilst the remaining two-thirds and trimethylene dibromide (50 g.) were simultaneously introduced from dropping-funnels over a period of ½ hour. The mixture was boiled for a further ½ hour, cooled, diluted, and extracted with ether (5 times). The ethereal solution was dried, and distilled through a Widmer column (the sulphide being volatile with ether) (Yield : 7—9 g.).

The dimethiodide, produced by keeping a mixture of the sulphide and an excess of methyl iodide for 24 hours, crystallised well from absolute ethyl alcohol; m. p. 97—98° (Found: I, 70·4. Calc.: I, 70·9%). The proportion of iodine found by precipitation with an excess of silver nitrate in cold aqueous solution was 33·3, 33·6, and 41·6% after 5, 15, and 120 minutes, respectively, whilst rapid titration gave a mean value of 33·3% (Calc. for one atom of iodine per molecule, 35·4%).

Action of Silver Chloride on the Iodide.—The iodide (1·7 g.) dissolved in cold water (25 c.c.) was shaken with freshly precipitated silver chloride (2 mols.) for 15 minutes, and the solution filtered. Addition of platinic chloride then precipitated a *chloroplatinate*, as an ochre-coloured powder which evolved much iodine on heating (Found: Pt, 22·7, 22·3. $C_{10}H_{24}Cl_6I_2S_2Pt$ requires Pt, 22·4%), and of auric chloride a *chloroaurate*, as a canary-yellow powder which evolved much iodine on ignition (Found: Au, 34·5. $C_5H_{12}Cl_4ISAu$ requires Au, 34·6%).

Attempts to isolate a crystalline picrate, mercuri-iodide, or oxalate were unsuccessful.

Action of Dimethylaniline on the Iodide.—When the iodide was heated at 100° with dimethylaniline (1 equiv. or more), a good yield of dimethylaniline methiodide, m. p. 215—217° (decomp.), was obtained (Found: I, 48·2. Calc.: I, 48·3%).

Synthesis of Dimethyl-γ-iodopropylsulphonium Iodide.—γ-Hydroxypropyl mercaptan (27 g.) was methylated by dissolving it in alkali (35 g. of sodium hydroxide in 150 c.c. of water) and adding methyl sulphate (44 g.). The mixture was heated at 100° for 1 hour, cooled, acidified with acetic acid, and extracted with ether. The extract was dried, evaporated, and finally fractionated under diminished pressure. *Methyl γ-hydroxypropyl sulphide* was thus obtained as a colourless oil, b. p. 102°/24 mm., $d_4^{20°}$ (vac.) 1·030 (Found: C, 45·05; H, 9·4. $C_4H_{10}OS$ requires C, 45·3; H, 9·4%). When this substance was dissolved in an excess of methyl iodide, heat was developed and an oil began at once to separate. After 6 hours, the excess of methyl iodide was decanted from the crude *dimethyl-γ-hydroxypropylsulphonium iodide*, which was not further purified. It was covered with dry xylene and dry hydrogen iodide was passed in at 100° for a short time. The xylene was then decanted, and the residue, when inoculated with a trace of the "dimethiodide" of trimethylene sulphide, crystallised at once. After crystallisation from alcohol, *dimethyl-γ-iodopropylsulphonium iodide* was obtained in colourless needles of m. p. 97·5°, not depressed by admixture of the "dimethiodide" of trimethylene sulphide

(Found: by precipitation in cold solution, I, 32·2; in boiling solution, 70·4. Calc.: I, 70·9%).

The authors wish to express their thanks to Mr. G. A. Birkett for translating the Russian memoir on which this work was based.

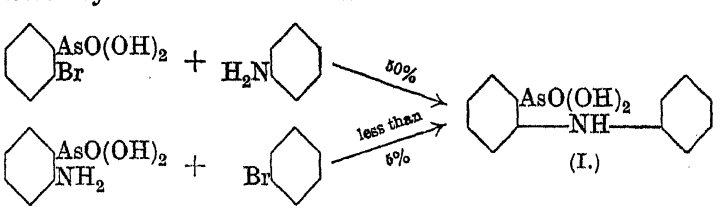
THE UNIVERSITY, SHEFFIELD. [*Received, August 11th*, 1927.]

CCCXXXV.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part V. The General Method of Synthesis and Determination of Constitution.*

By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

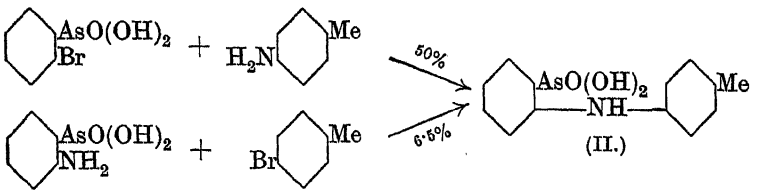
IT has been shown (J., 1927, 247) that carboxy-derivatives of 10-chloro-5 : 10-dihydrophenarsazine which are not accessible by the condensation of arsenious chloride with the corresponding substituted diphenylamines may be prepared by condensing *o*-bromophenylarsinic acid with aminobenzoic acids and subsequent ring closure. Further, it was shown (J., 1926, 2243) that certain substituted diphenylamines will not condense with arsenious chloride, although where at least two of the four ortho-positions in diphenylamine are unoccupied, there seemed reason to believe that the corresponding phenarsazine derivative should be capable of existence. By investigating in greater detail the conditions of the formation of various arsinic acids derived from diphenylamine and the conditions of ring closure to form the heterocyclic arsenic compound, it has been possible to study the properties of some of the compounds hitherto unprepared and to throw more light on the constitution of some already known compounds belonging to this series.

The preparation of *diphenylamine*-o-*arsinic acid* (I) has been effected by two methods as indicated:

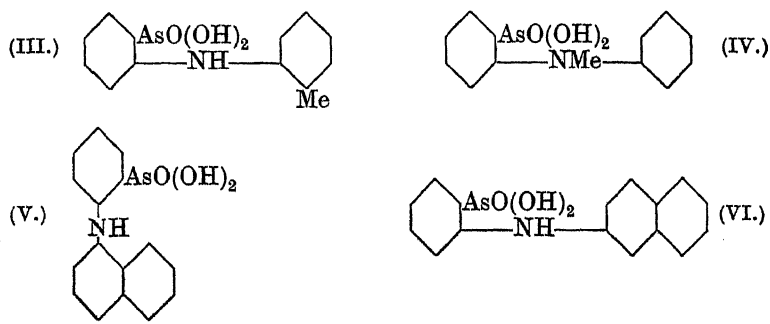


The condensations were carried out under identical conditions and it will be seen that the yield of the condensation product varied

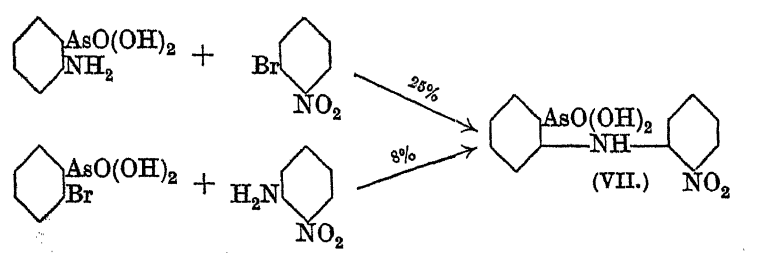
very considerably according as *o*-bromophenylarsinic acid or *o*-aminophenylarsinic acid was the initial material. A result of the same kind was obtained in the preparation by two methods of 4-*methyldiphenylamine*-6′-*arsinic acid* (II):



Since, in both cases, the use of *o*-bromophenylarsinic acid gave a higher yield of the desired arsinic acid, 2-*methyldiphenylamine*-6′-*arsinic acid* (III) (23% yield), N-*methyldiphenylamine*-o-*arsinic acid* (IV) (28% yield), 2-α-*naphthylaminophenylarsinic acid* (V) (81% yield), and 2-β-*naphthylaminophenylarsinic acid* (VI) (90% yield) were readily obtained by condensing *o*-bromophenylarsinic acid with the corresponding amine.

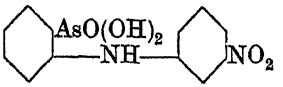
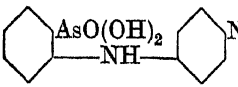


In the case of the production of 2-*nitrodiphenylamine*-6′-*arsinic acid* (VII), the higher yield was obtained when *o*-aminophenyl-



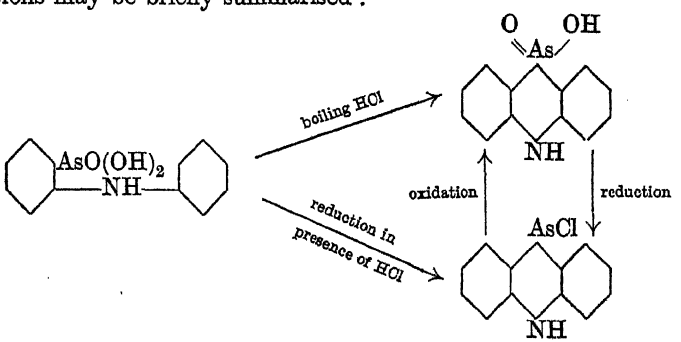
arsinic acid was used, and hence for the preparation of 3-*nitrodiphenylamine*-6′-*arsinic acid* (VIII) and of 4-*nitrodiphenylamine*-

6′-*arsinic acid* (IX), *o*-aminophenylarsinic acid was condensed with the corresponding bromonitrobenzene.

(VIII.)   (IX.)

These results would indicate that the ease with which the reaction proceeds depends on the reactivity of the bromine atom, being slight in bromobenzene, greatest in *o*-bromonitrobenzene, and intermediate in the case of *o*-bromophenylarsinic acid.

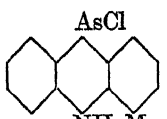
With the exception of *N*-methyldiphenylamine-*o*-arsinic acid (IV), all the above acids can be converted into the corresponding heterocyclic arsenic compounds. Diphenylamine-*o*-arsinic acid (I), when boiled with concentrated hydrochloric acid, is converted rapidly first into an oil and then into the previously described hydrochloride of phenarsazinic acid (J., 1924, **125**, 2277). The same acid, when reduced by the alcohol–iodine–hydrochloric acid–sulphur dioxide method, is rapidly converted into 10-chloro-5 : 10-dihydrophenarsazine, which again can be oxidised to phenarsazinic acid. Incidentally, 10-chloro-5 : 10-dihydrophenarsazine has thus again been synthesised by a simpler method and its constitution further verified (compare Burton and Gibson, J., 1926, 452). These reactions may be briefly summarised :

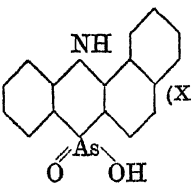


When 4-methyldiphenylamine-6′-arsinic acid (II) was boiled with concentrated hydrochloric acid, similar effects were observed and the already described hydrochloride of 2-methylphenarsazinic acid (J., 1926, 469) was readily obtained. Also, by reduction with sulphur dioxide under the usual conditions, 10-chloro-2-methyl-5 : 10-dihydrophenarsazine was produced, which again was easily oxidised to the heterocyclic arsinic acid. Ring closure also took place on boiling the acid (II) with acetic anhydride. The synthesis of 10-chloro-2-methyl-5 : 10-dihydrophenarsazine has thus been effected and, incidentally, the *hydrobromide* of 2-methylphenarsazinic

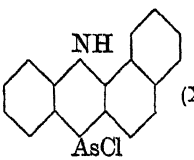
acid was prepared from the acid (II) by using hydrobromic acid instead of hydrochloric acid, and 10-*bromo*-2-*methyl*-5 : 10-*dihydrophenarsazine* was obtained from the acid (II) or from the corresponding phenarsazinic acid in the usual way.

Although the corresponding ring closure by means of hydrochloric acid took an appreciably longer time, 2-methyldiphenylamine-6′-arsinic acid (III) was converted into 4-*methylphenarsazinic acid hydrochloride* and 4-*methylphenarsazinic acid*. From both 2-methyldiphenylamine-6′-arsinic acid and 4-methylphenarsazinic acid, 10-*chloro*-4-*methyl*-5 : 10-*dihydrophenarsazine* (X) and also the corresponding *bromo*-compound have been prepared for the first time, since phenyl-*o*-tolylamine was not available when the condensation of arsenious chloride with various diphenylamines was being investigated.

(X.) 



(XI.)

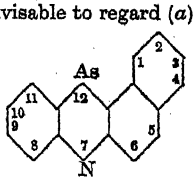


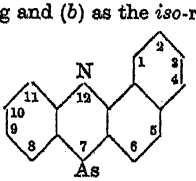
(XII.)

The formation of heterocyclic arsenic compounds from 2-α-naphthylaminophenylarsinic acid (V) can be accomplished very easily.

7 : 12-iso*Benzophenarsazinic acid* (XI) is easily produced by boiling the original acid for two minutes with concentrated hydrochloric acid containing a little alcohol, while the already described 7-chloro-7 : 12-dihydro*iso*benzophenarsazine * (XII) (Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218; Burton and Gibson, J., 1926, 467) is obtained very readily by the usual method of reduction. This synthesis effectively proves the correctness of the constitution assigned to the product of condensation of arsenious chloride and phenyl-α-naphthylamine.

* Previously called 7-chloro-7 : 12-dihydrobenzophenarsazine. It is considered advisable to regard (*a*) as the normal ring and (*b*) as the *iso*-ring, since

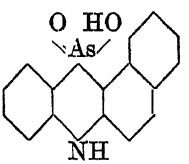
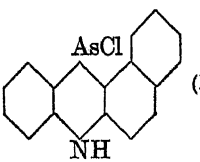
(*a*) 



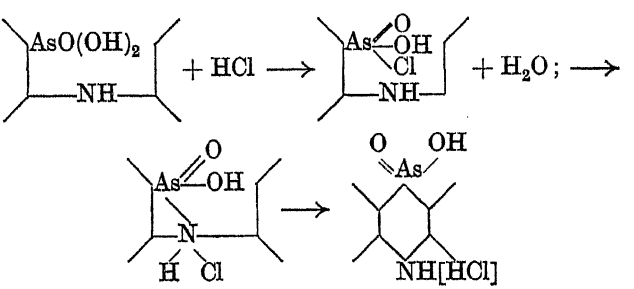
(*b*)

in (*b*) the hetero-atoms have to be numbered inversely to their accepted order on account of the geometry of the ring. This will avoid any confusion in the naming of the parent substances. The parent substance of compound (XII) will be 7 : 12-dihydro*iso*benzophenarsazine and of compound (XIV), 7 : 12-dihydrobenzophenarsazine.

The formation of the corresponding heterocyclic arsenic compounds from 2-β-naphthylaminophenylarsinic acid (VI) was just as readily accomplished. The *hydrochloride* of 7 : 12-*benzophenarsazinic acid* or the free acid (XIII) was readily produced by boiling 2-β-naphthylaminophenylarsinic acid with concentrated hydrochloric acid containing a little alcohol or by boiling it with acetic acid. Further, the previously described 12-chloro-7 : 12-dihydrobenzophenarsazine (XIV) (Burton and Gibson,* J., 1926, 2241) was easily obtained by the usual method of reduction from either 2-β-naphthylaminophenylarsinic acid or from the heterocyclic acid (XIII). On the assumption that the condensation goes in the α-position of the naphthalene nucleus, the constitution assigned previously to the condensation product of arsenious chloride and phenyl-β-naphthylamine is verified by the present work.

(XIII.)   (XIV.)

In several of the above cases when the ring closure was effected by boiling hydrochloric acid, an oily intermediate product possessing a characteristic acid chloride-like odour was formed prior to the formation of the crystalline hydrochloride of the heterocyclic arsinic acid. Although this intermediate product was never isolated, its repeated formation led us to believe that the condensation is preceded by the formation of an acid chloride and we suggest that the following scheme may represent the formation of the hydrochloride of the phenarsazinic acid :

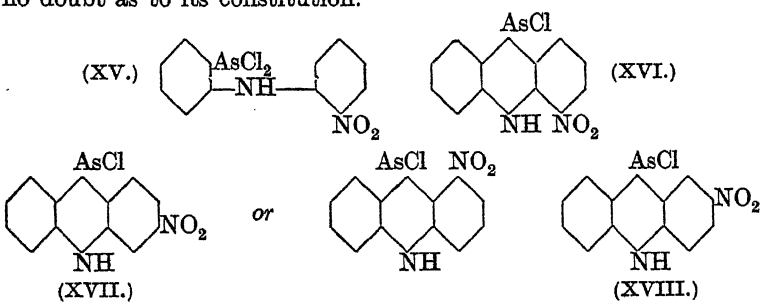


When ring closure was effected by the alcohol–hydrochloric acid–iodine–sulphur dioxide method, in none of the above cases were

* There is a misprint on p. 2243 (line 4 from bottom) : " 12-chloro-7 : 12-dihydrophenarsazine " should be " 12-chloro-7 : 12-dihydrobenzophenarsazine."

we able to isolate the intermediate dichloroarsine; indeed, in only one case (described below) has this been possible.

When 2-nitrodiphenylamine-6′-arsinic acid (VII) was reduced for 5 minutes with sulphur dioxide in the presence of alcoholic hydrochloric acid and a trace of iodine, an oil was formed which, after solidification and recrystallisation, was obtained as deep red crystals of 2-*nitrodiphenylamine*-6′-*dichloroarsine* (XV), from which the original acid was regenerated by oxidation with hydrogen peroxide in acetic acid solution. When the dichloroarsine was boiled in acetic acid solution for 3 hours, 10-*chloro*-4-*nitro*-5 : 10-*dihydrophenarsazine* (XVI) crystallised in characteristic scarlet needles, m. p. 165°. The method of production of this compound leaves no doubt as to its constitution.



In the reduction of 3-nitrodiphenylamine-6′-arsinic acid (VIII) no intermediate dichloroarsine was obtained. From its method of formation, however, the homogeneous compound must be 10-*chloro*-3(or 1)-*nitro*-5 : 10-*dihydrophenarsazine* (XVII) and it was obtained in deep red, prismatic needles, m. p. 258—259° (decomp.). The corresponding 3(or 1)-*nitrophenarsazinic acid* and the 10-*bromo*-3(or 1)-*nitro*-5 : 10-*dihydrophenarsazine* were also isolated. [Previous work (J., 1926, 2241; compare Roberts and Turner, J., 1925, **127**, 2005) clearly suggests that the nitro-group in these compounds is probably in the 3 position.]

When 4-nitrodiphenylamine-6′-arsinic acid (IX) was reduced under similar conditions, no dichloroarsine was isolated, but there was no difficulty in isolating 10-*chloro*-2-*nitro*-5 : 10-*dihydrophenarsazine* (XVIII), m. p. 278° (decomp.), and the method of preparation leaves no doubt as to the constitution of this substance.

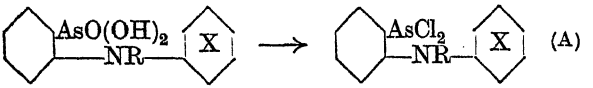
The synthesis and identification of these three nitro-derivatives have enabled us to clear up certain obscurities in the previous work on compounds of this series. 10-Chloro-4-nitro-5 : 10-dihydrophenarsazine (XVI) has been oxidised to the corresponding acid, and this reduced by ferrous hydroxide to the hydrochloride of 4-aminophenarsazinic acid, identical with the compound prepared

by Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1). Although we expected a triazo-derivative might be formed, this compound is unaffected by nitrous acid at 5°.

Wieland and Rheinheimer obtained two mononitro-derivatives by the nitration of 10-chloro-5 : 10-dihydrophenarsazine. They concluded that the one produced in less quantity (brilliant scarlet needles) had the nitro-group in the ortho-position to the :NH group and although the melting point recorded by them is somewhat low (156°), the description shows that the compound actually was 10-chloro-4-nitro-5 : 10-dihydrophenarsazine (XVI), now synthesised and obtained by us in a pure condition, m. p. 165°. The other mononitro-derivative, Wieland and Rheinheimer rightly concluded was the para-isomeride, *viz.*, 10-chloro-2-nitro-5 : 10-dihydrophenarsazine (XVIII). They described it as crystallising in greenish-yellow scales, but did not record any melting point. On carefully repeating their work, we found that this compound was identical with the synthesised substance (XVIII), m. p. 278° (decomp.). Wieland and Rheinheimer further stated that this compound on oxidation was converted into the nitrophenarsazinic acid (the 2-nitro-acid) which is the by-product of the nitration of phenarsazinic acid, the main product, according to them, being 4-nitrophenarsazinic acid. We have found, however, that the main (*i.e.*, the more easily isolated) product of the nitration of phenarsazinic acid under the conditions described by Wieland and Rheinheimer is the 2-nitro-acid, for on repeating their work we isolated an acid which, on reduction by the sulphur dioxide–alcohol–hydrochloric acid–iodine method, gave 10-chloro-2-nitro-5 : 10-dihydrophenarsazine (XVIII) in a slightly impure form. Moreover, Burton and Gibson's "1-nitrophenarsazinic acid" (*loc. cit.*, p. 2243) is actually the 2-nitro-acid, for it gives the substance (XVIII) on reduction. As a result of the work now described, the conclusions drawn by Burton and Gibson as to the constitution of the corresponding amino-derivatives must be modified accordingly.

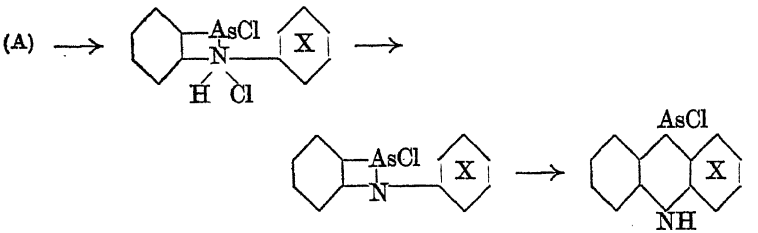
In view of the previous failure to prepare 10-chloro-5-methyl-5 : 10-dihydrophenarsazine (Burton and Gibson, J., 1926, 453; compare Wieland and Rheinheimer, *loc. cit.*), it is interesting to know that normal ring closure does not take place when *N*-methyldiphenylamine-*o*-arsinic acid (IV) is submitted to any of the treatments mentioned above for this purpose. Indeed, the only product which we have isolated by the alcohol–hydrochloric acid–iodine–sulphur dioxide reduction method was somewhat impure 10-chloro-5 : 10-dihydrophenarsazine in small quantity (compare Burton and Gibson, *loc. cit.*). Whilst we have again been unsuccessful in preparing 10-chloro-5-methyl-5 : 10-dihydrophenarsazine, the results

of the work indicate that ring closure effected by reduction by the sulphur dioxide method probably follows the course

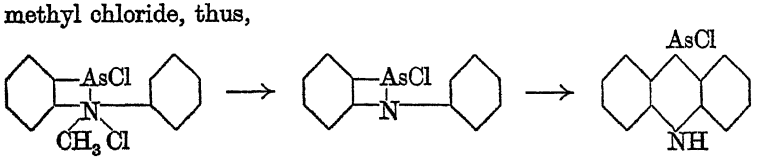


(A)

Where R = H and X(*o*- or *p*-) = H or Me,



If X = NO_2 and R = H, the nitrogen atom will be less basic and arsenic–nitrogen ring closure will tend to take place with less ease, especially in the case of the 2-nitro-compound (VII). In this case we have actually isolated the dichloroarsine and it is possible that steric hindrance here plays some part (compare Roberts and Turner, *loc. cit.*). If R = Me and X = H, there will be less tendency for arsenic–nitrogen ring closure to take place. The small amount of the product of such ring closure will not be stable and should lose methyl chloride, thus,



with the formation of a small quantity of 10-chloro-5:10-dihydrophenarsazine, as found experimentally.

EXPERIMENTAL.

The method previously described for the preparation of *o*-bromophenylarsinic acid (J., 1926, 456) has been considerably modified, whereby a higher yield (56%) is obtained and economy in hydrobromic acid effected. *o*-Aminophenylarsinic acid (150 g.), dissolved in concentrated hydrochloric acid (210 c.c.) and water (210 c.c.), was diazotised below 5° with sodium nitrite (50 g.; water, 110 c.c.). Cuprous bromide (copper sulphate crystals, 150 g., in water, 500 c.c.; potassium bromide, 75 g., in water, 175 c.c.; the solution was reduced with sulphur dioxide, and the precipitate filtered off and washed with water) was dissolved in hydrobromic acid (of constant b. p.; 270 c.c.) and to this solution at the ordinary tem-

perature the diazo-solution was added with constant stirring. After stirring for 1 hour, the precipitated acid was dissolved in sodium hydroxide solution, and the solution was decolorised with charcoal and acidified with hydrochloric acid (Congo-red). The colourless crystals had m. p. 199—200° (decomp.).

o-Bromonitrobenzene may be obtained in 86% yield by the following modification of Ullmann's method (*Ber.*, 1896, **29**, 1880). *o*-Nitroaniline (138 g.), dissolved in concentrated hydrochloric acid (215 c.c.) and water (128 c.c.), was diazotised below 10° with sodium nitrite (75 g. in water, 150 c.c.). A solution of cuprous bromide in hydrobromic acid (of constant b. p.; 320 c.c.) was prepared from copper sulphate crystals (193 g. in water, 640 c.c.) and potassium bromide (96·5 g. in water, 210 c.c.) as described above, and the diazo-solution added to it at the ordinary temperature with constant stirring. The *o*-bromonitrobenzene, m. p. 43—44°, was isolated by steam distillation.

Diphenylamine-o-arsinic Acid, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2$ (I).—(*a*) A mixture of aniline (4·7 g.), *o*-bromophenylarsinic acid (14 g.), dry potassium carbonate (9·3 g.), amyl alcohol (38 c.c.), and a trace of copper powder was boiled for 5 hours. The volatile substances were removed by steam distillation and the residue was decolorised with charcoal. The filtrate on acidification with hydrochloric acid deposited a dark-coloured solid (7·1 g.), which was recrystallised from glacial acetic acid and then from dilute acetic acid.

(*b*) A mixture of bromobenzene (6·0 g.), *o*-aminophenylarsinic acid (6·75 g.), dry potassium carbonate (6·0 g.), amyl alcohol (35 c.c.), and a trace of copper powder was treated in a similar manner. Only 0·4 g. of product was obtained.

Diphenylamine-o-arsinic acid forms colourless, felted needles, m. p. 166° (slight decomp.). It cannot be titrated with 0·1*N*-sodium hydroxide and phenolphthalein, the end-point varying with the concentration; but its basicity is greater than unity (Found: As, 25·5. $C_{12}H_{12}O_3NAs$ requires As, 25·6%).

Conversion of Diphenylamine-o-arsinic Acid into Phenarsazinic Acid and 10-Chloro-5 : 10-dihydrophenarsazine.—(*a*) Diphenylamine-*o*-arsinic acid (1 g., either crude or pure) was boiled with concentrated hydrochloric acid (7 c.c.). An oil having a characteristic odour was first formed, but it rapidly disappeared and after 2 minutes' boiling the liquid became filled with crystals of phenarsazinic acid hydrochloride identical with an authentic specimen, m. p. 203—205° (decomp.). This hydrochloride dissolved in an excess of aqueous sodium hydroxide, from which solution phenarsazinic acid was precipitated on addition of acetic acid. The phenarsazinic acid was dissolved in hot alcohol–hydrochloric acid

and reduced with sulphur dioxide after addition of a trace of iodine. 10-Chloro-5:10-dihydrophenarsazine, m. p. 191°, identical with an authentic specimen, was obtained (Found: Cl, 12·9. Calc.: Cl, 12·8%).

(*b*) Diphenylamine-*o*-arsinic acid (1 g., either crude or pure), dissolved in a hot mixture of alcohol (5 c.c.) and concentrated hydrochloric acid (5 c.c.), deposited 10-chloro-5:10-dihydrophenarsazine, m. p. 191° (after recrystallisation from benzene), on reduction with sulphur dioxide after addition of a trace of iodine. The chloro-compound, on oxidation with chloramine-T in aqueous acetone (Burton and Gibson, J., 1924, **125**, 2276), was converted into phenarsazinic acid.

4-*Methyldiphenylamine*-6′-*arsinic Acid*,

$$C_6H_4Me{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2 \quad (II).$$

—(*a*) The product obtained from *p*-toluidine (4·9 g.) and *o*-bromophenylarsinic acid (12·9 g.), worked up as described above, amounted to 10 g. (*b*) The amount obtained from *p*-bromotoluene (8·6 g.) and *o*-aminophenylarsinic acid (10·9 g.) was only 1·0 g. Pure 4-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 160—165° (decomp.), was obtained as a cream-coloured solid by recrystallising the product from dilute acetic acid (Found: As, 24·1. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). It is soluble in hot alcohol or hot glacial acetic acid and only slightly soluble in water.

4-Methyldiphenylamine-6′-arsinic acid (10 g. of crude acid) was boiled with concentrated hydrochloric acid (40 c.c.). An oil was formed and the mixture vigorously stirred during the heating. After about 2 minutes the solution became homogeneous and then suddenly filled with crystals (8·5 g.) of 2-methylphenarsazinic acid hydrochloride, m. p. 200—204° (decomp.), which was identical with an authentic specimen (J., 1926, 469). On treatment with sodium hydroxide, the sodium salt, which is sparingly soluble in cold water, was obtained, and from this 2-methylphenarsazinic acid, m. p. 306° (decomp.), was isolated by acidification with glacial acetic acid. This was identical with a specimen made by oxidising the condensation product of arsenious chloride and phenyl-*p*-tolylamine. The hydrochloride, m. p. 208° (decomp.), was readily re-formed on dissolving the acid in a hot mixture of equal volumes of alcohol and concentrated hydrochloric acid and allowing the solution to cool (Found: Cl, 11·2. Calc.: Cl, 10·9%).

A boiling solution of 4-methyldiphenylamine-6′-arsinic acid (1 g.) in alcohol (7 c.c.) and concentrated hydrochloric acid (7 c.c.) containing a trace of iodine was treated with sulphur dioxide; reduction was complete after 5 minutes. The product, recrystallised from benzene, gave 10-chloro-2-methyl-5:10-dihydrophenarsazine

in orange-yellow needles, m. p. 199—200°, which did not depress the melting point of an authentic specimen (Found: Cl, 12·2. Calc.: Cl, 12·2%). On oxidation with chloramine-T in aqueous acetone, it was converted into the colourless 2-methylphenarsazinic acid, m. p. 306—308° (decomp.), identical with an authentic specimen.

4-Methyldiphenylamine-6′-arsinic acid (3 g.) was boiled with acetic anhydride (15 c.c.) for 2 hours. The solution remaining after half of the anhydride had been distilled off was deep blue and deposited 0·6 g. of colourless, crystalline material. This was washed with alcohol and had m. p. 308° (decomp.). On reduction with sulphur dioxide under the usual conditions, it was converted into 10-chloro-2-methyl-5 : 10-dihydrophenarsazine. 2-Methylphenarsazinic acid under the same conditions was not acetylated.

2-*Methylphenarsazinic acid hydrobromide*,

$$NH\langle\begin{matrix}C_6H_3Me\\C_6H_4\end{matrix}\rangle AsO(OH),HBr,$$

was prepared by dissolving 2-methylphenarsazinic acid (1 g.) in a hot mixture of alcohol (5 c.c.) and hydrobromic acid (of constant b. p.; 6 c.c.) and allowing the solution to cool. It crystallised as an almost colourless, granular powder, which turned orange-coloured on heating above 100° and had m. p. 208—210° (decomp.) (Found: Br, 21·3. $C_{13}H_{13}O_2NBrAs$ requires Br, 21·6%). It was also formed by boiling 4-methyldiphenylamine-6′-arsinic acid (1 g.) with hydrobromic acid (of constant b. p.; 8 c.c.) for a few minutes, but the reaction did not take place so smoothly as in the formation of the hydrochloride: the tarry matter formed was removed by washing the precipitate with a mixture of hydrobromic acid and alcohol.

10-*Bromo*-2-*methyl*-5 : 10-*dihydrophenarsazine*,

$$NH\langle\begin{matrix}C_6H_3Me\\C_6H_4\end{matrix}\rangle AsBr,$$

was prepared by dissolving 2-methylphenarsazinic acid or 4-methyldiphenylamine-6′-arsinic acid (1 g.) in a hot mixture of alcohol (5 c.c.) and hydrobromic acid (of constant b. p.; 5 c.c.) and reducing the product in the usual way; it crystallised from benzene in rosettes of hard, orange-red needles, m. p. 180° (decomp.) (Found: Br, 23·9. $C_{13}H_{11}NBrAs$ requires Br, 23·8%).

2-*Methyldiphenylamine*-6′-*arsinic Acid*,

$$C_6H_4Me\cdot NH\cdot C_6H_4\cdot AsO(OH)_2 \text{ (III)}.$$

—*o*-Toluidine (15 g.), *o*-bromophenylarsinic acid (39 g.), dry potassium carbonate (30 g.), amyl alcohol (120 c.c.), and a trace of copper powder were boiled for 7 hours and worked up as before. On acidifying the solution of the potassium salt, 2-methyldiphenyl-

amine-6′-arsinic acid (10 g.) was obtained as a light cream-coloured solid. It was difficult to purify, but from dilute acetic acid it was obtained as a slightly discoloured solid of indefinite melting point (130—140°) (Found: As, 24·2. $C_{13}H_{14}O_3NAs$ requires As, 24·4%).

4-*Methylphenarsazinic acid hydrochloride* was formed on boiling the preceding compound (crude) with concentrated hydrochloric acid as described for the isomeride, but the time elapsing before the separation of the hydrochloride was almost twice as long. The crude salt had m. p. 187—189° (decomp.). 4-*Methylphenarsazinic acid* was formed from the crude hydrochloride by treatment with an excess of sodium hydroxide solution and then acidification with acetic acid. The precipitated acid was recrystallised from dilute acetic acid and then had m. p. 309—310° (decomp.) (Found: As, 25·7. $C_{13}H_{12}O_2NAs$ requires As, 25·9%). This acid tends to form an unstable acetate, since, when it was recrystallised from glacial acetic acid and air-dried for 2 days, it still retained 5·61% of acetic acid (Calc. for 1 mol. of $C_2H_4O_2$, 17·2%). 4-Methylphenarsazinic acid resembles the 2-isomeride in most of its properties: the sodium salt is not very soluble in cold water and it is readily converted into the *hydrochloride*, colourless needles, m. p. 199° (decomp.), by the usual method (Found: Cl, 10·9. $C_{13}H_{13}O_2NClAs$ requires Cl, 10·9%).

10-*Chloro*-4-*methyl*-5:10-*dihydrophenarsazine* (X). — 4-Methylphenarsazinic acid or crude 2-methyldiphenylamine-6′-arsinic acid was reduced as described for the 2-isomeride. Recrystallised from benzene, the product formed yellow needles (occasionally greenish-yellow), m. p. 191° (decomp.). The yield was almost quantitative (Found: Cl, 12·3. $C_{13}H_{11}NClAs$ requires Cl, 12·2%).

10-*Bromo*-4-*methyl*-5:10-*dihydrophenarsazine* was prepared in an analogous manner from 4-methylphenarsazinic acid. It was recrystallised from benzene and obtained in light yellow needles, m. p. 190° (slight decomp.) (Found: Br, 24·0. $C_{13}H_{11}NBrAs$ requires Br, 23·8%). Both these compounds were converted into 4-methylphenarsazinic acid on oxidation with chloramine-T in aqueous acetone.

N-*Methyldiphenylamine*-o-*arsinic Acid* (IV).—Monomethylaniline* (15 g.), *o*-bromophenylarsinic acid (39 g.), dry potassium carbonate (30 g.), amyl alcohol (120 c.c.), and a trace of copper powder were boiled for 5 hours. The product was worked up in the usual manner, and the N-*methyldiphenylamine*-o-*arsinic acid* (12 g.) obtained as a colourless, crystalline solid, m. p. 182—184°

* Purified through its *p*-toluenesulphonyl derivative. It had b. p. 196°/764 mm., and gave quantitative yields of its acetyl and *p*-toluenesulphonyl derivatives (m. p.'s 101° and 94°, respectively).

(decomp.) after recrystallisation from dilute acetic acid. It was difficult to purify (Found: As, 24·2. $C_{13}H_{14}O_3NAs$ requires As, 24·4%). Boiling with concentrated hydrochloric acid for 5 minutes caused no separation of crystalline matter, but some decomposition took place and the characteristic odour, which we attribute to the intermediate formation of an acid chloride, was observed. On cooling, treatment with sodium hydroxide, and acidification with acetic acid, only an impure acid was precipitated. When hydrobromic acid was used instead of hydrochloric acid, marked decomposition took place.

N-Methyldiphenylamine-*o*-arsinic acid (8 g.) was reduced in hot alcoholic-concentrated hydrochloric acid solution in the manner already described, but the product of the reduction was a heavy, dark-coloured oil. A small amount of yellowish-brown solid separated from the oily matter on cooling. This was recrystallised from benzene and melted at 175—177°. The melting point was raised (187—188°) by admixture with pure 10-chloro-5 : 10-dihydrophenarsazine, but the quantity obtained was too small for further purification and attempts to work up the oil were unavailing. 10-Chloro-5-methyl-5 : 10-dihydrophenarsazine therefore cannot be prepared by this method and it was also found impossible to prepare the corresponding bromo-compound.

2-α-*Naphthylaminophenylarsinic Acid* (V).—On mixing α-naphthylamine (16·0 g.), *o*-bromophenylarsinic acid (28·2 g.), dry potassium carbonate (19·0 g.), amyl alcohol (80 c.c.), and a trace of copper powder an almost solid mass was produced. The mixture was boiled for 6½ hours and the product isolated (28 g., crude) in the usual way. The acid recrystallised from dilute acetic acid had m. p. 165° (Found: As, 21·6. $C_{16}H_{14}O_3NAs$ requires As, 21·9%).

2-α-Naphthylaminophenylarsinic acid (10 g.) was dissolved as rapidly as possible in a hot mixture of alcohol (50 c.c.) and concentrated hydrochloric acid (50 c.c.) and reduced with sulphur dioxide after addition of a trace of iodine. The precipitated 7-*chloro*-7 : 12-*dihydroisobenzophenarsazine* (XII) was filtered off from the cold liquid and recrystallised from toluene. The short, yellow needles, m. p. 219°, were identical with an authentic specimen (Found: Cl, 10·7. $C_{16}H_{11}NClAs$ requires Cl, 10·8%).

7 : 12-iso*Benzophenarsazinic Acid Hydrochloride*.—2-α-Naphthylaminophenylarsinic acid (3·5 g.) was dissolved in a mixture of alcohol (15 c.c.) and concentrated hydrochloric acid (15 c.c.), and the mixture rapidly heated on the water-bath. After 2 minutes and while the solution was still hot, small, colourless plates of the *hydrochloride* of 7 : 12-*iso*benzophenarsazinic acid began to separate. It has m. p. 232° (decomp.) (Found: Cl, 10·0. $C_{16}H_{13}O_2NClAs$

requires Cl, 9·8%). This, on treatment with warm dilute sodium hydroxide solution followed by acidification with acetic acid, was converted into colourless 7:12-*iso*benzophenarsazinic acid (XI), which was recrystallised from dilute acetic acid (Found: As, 22·9. Calc.: As, 23·1%). The sodium salt had the properties described by Lewis and Hamilton (*J. Amer. Chem. Soc.*, 1921, **43**, 2218).

2-β-*Naphthylaminophenylarsinic Acid* (VI).—β-Naphthylamine was condensed with *o*-bromophenylarsinic acid, the quantities taken and the conditions of the reaction being the same as in the preparation of the isomeric substance. The crude acid (31 g.) was deposited in colourless needles, m. p. 181°, after the solution in hot alcohol had been decolorised with charcoal (Found: As, 21·6. $C_{16}H_{14}O_3NAs$ requires As, 21·9%). 12-Chloro-7:12-dihydrobenzophenarsazine (XIV) was prepared from this compound (10 g.) by the method used for the preparation of the isomeride. It was recrystallised from *s*-tetrachloroethane and obtained in yellow leaflets, m. p. 254°, identical in every respect with the compound formed by the condensation of arsenious chloride with phenyl-β-naphthylamine. Yield, 7 g. (Found: Cl, 10·85. Calc.: Cl, 10·8%).

7:12-*Benzophenarsazinic Acid* (XIII).—When a solution of the preceding compound (25 g.) in hot glacial acetic acid (200 c.c.) was rapidly cooled and treated with hydrogen peroxide (20 vols.; 130 c.c.) and then heated almost to boiling to complete the oxidation, 7:12-benzophenarsazinic acid was precipitated as a brown, amorphous solid. It was recrystallised from dilute acetic acid after decoloration with charcoal and obtained in small, colourless needles, m. p. above 325°. Yield, 18 g. (Found: As, 22·8. $C_{16}H_{12}O_2NAs$ requires As, 23·1%). The same acid was produced when a solution of 12-chloro-7:12-dihydrobenzophenarsazine was oxidised with an aqueous solution of chloramine-T. It was also obtained when a solution of 2-β-naphthylaminophenylarsinic acid in the minimum quantity of boiling glacial acetic acid was heated on the water-bath for 30 minutes. The acid crystallised on cooling and the filtrate contained a small quantity of unchanged 2-β-naphthylaminophenylarsinic acid.

7:12-*Benzophenarsazinic acid hydrochloride* was obtained by dissolving 2-β-naphthylaminophenylarsinic acid (0·3 g.) in a hot mixture of alcohol (5 c.c.) and concentrated hydrochloric acid (5 c.c.). After a few minutes the compound, m. p. 234° (decomp.), separated in fine needles (Found: Cl, 10·0. $C_{16}H_{13}O_2NClAs$ requires Cl, 9·8%). It was converted into 7:12-benzophenarsazinic acid in the usual way. The sodium salt (colourless needles) of 7:12-benzophenarsazinic acid is not very soluble in cold water;

the ammonium salt crystallises in glistening plates from water; the barium, silver, and mercuric salts are produced as heavy, white precipitates; the ferric salt is brown and somewhat gelatinous; the copper salt is pale greenish-blue; the cobalt salt is pale blue, and the calcium salt forms fine, colourless needles.

12-*Bromo*-7 : 12-*dihydrobenzophenarsazine* was prepared by reducing 7 : 12-benzophenarsazinic acid in alcohol–hydrobromic acid solution in the usual way. It forms short, deep orange-coloured needles, m. p. 251—252° (decomp.), from toluene (Found : Br, 21·7. $C_{16}H_{11}NBrAs$ requires Br, 21·5%).

2-*Nitrodiphenylamine*-6′-*arsinic Acid* (VII). — A mixture of *o*-aminophenylarsinic acid (47·2 g.), *o*-bromonitrobenzene (49·0 g.), dry potassium carbonate (42 g.), amyl alcohol (245 c.c.), and a trace of copper powder was boiled for 6 hours. The product was worked up as usual, washed with dilute hydrochloric acid and water to remove unchanged *o*-aminophenylarsinic acid, and recrystallised from aqueous alcohol, forming golden-yellow needles, m. p. 238—240° (decomp.). Yield of pure acid, 25% (Found : N, 7·95. $C_{12}H_{11}O_5N_2As$ requires N, 8·3%). *o*-Bromophenylarsinic acid and *o*-nitroaniline, condensed in a similar manner, gave a 7·7% yield of the same product.

The acid is slightly soluble in water and is soluble in alcoholic hydrochloric acid, but a hydrochloride could not be isolated. Solutions of the sodium and potassium salts are deep red in contrast to that of the acid, which is deep yellow.

2-*Nitrodiphenylamine*-6′-*dichloroarsine* (XV).—The preceding compound (3·1 g.) was dissolved in a hot mixture of alcohol (20 c.c.) and concentrated hydrochloric acid (25 c.c.), and sulphur dioxide passed into the solution for 5 minutes only, after addition of a trace of iodine. The oil which separated quickly solidified on cooling. The solid crystallised from benzene–light petroleum (b. p. 60—80°) in deep red crystals, m. p. 110° (Found : Cl, 19·95. $C_{12}H_9O_2N_2Cl_2As$ requires Cl, 19·8%). On oxidation with hydrogen peroxide (20 vol.) in acetic acid solution, the above 2-nitrodiphenylamine-6′-arsinic acid was obtained.

10-*Chloro*-4-*nitro*-5 : 10-*dihydrophenarsazine* (XVI).—After a solution of 2-nitrodiphenylamine-6′-dichloroarsine (1·5 g.) in glacial acetic acid (25 c.c.) had been boiled for 3 hours, beautiful scarlet needles of 10-chloro-4-nitro-5 : 10-dihydrophenarsazine were deposited on cooling. It was recrystallised from glacial acetic acid and then had m. p. 165° (Wieland and Rheinheimer, *loc. cit.*, give m. p. 156°) (Found : Cl, 10·8. Calc. : Cl, 11·0%).

This compound was oxidised by hydrogen peroxide (20 vol.) in glacial acetic acid solution, whereby it was converted into 4-nitro-

phenarsazinic acid. This acid was reduced by ferrous hydroxide (Burton and Gibson, *loc. cit.*) and converted into the 4-aminophenarsazinic acid, which was conveniently isolated as the hydrochloride. The hydrochloride, suspended in excess of dilute hydrochloric acid, was unaffected by sodium nitrite at 5°.

3-*Nitrodiphenylamine*-6'-*arsinic acid* (VIII) was prepared from *o*-aminophenylarsinic acid (20·9 g.) and *m*-bromonitrobenzene (21·7 g.) in a similar manner to the isomeride, the boiling, however, being continued for 7 hours. The product (16 g.) crystallised from dilute acetic acid in light yellow needles, m. p. 202° (decomp.) (Found: As, 21·7. $C_{12}H_{11}O_5N_2As$ requires As, 22·2%). The solutions of the sodium and potassium salts are deep red.

10-*Chloro*-3(or 1)-*nitro*-5:10-*dihydrophenarsazine* (XVII).—The compound just described (20 g.) was reduced in the usual manner for 15 minutes by sulphur dioxide; a deep red, crystalline substance soon filled the liquid. The product was fractionally crystallised from glacial acetic acid and only one substance, which formed glistening, thin prisms, m. p. 258—259° (decomp.), was obtained (Found: As, 22·8; Cl, 11·2. $C_{12}H_8O_2N_2ClAs$ requires As, 23·2; Cl, 11·0%).

3(or 1)-*Nitrophenarsazinic Acid*.—The preceding compound (4 g.) was boiled with glacial acetic acid (60 c.c.) and rapidly cooled, and to the solution-suspension hydrogen peroxide (20 vol.; 40 c.c.) was added. The colour of the solution rapidly changed and a yellowish-brown acid was precipitated; the reaction was completed by gentle warming. The product was recrystallised from dilute acetic acid. The yellow substance did not melt below 320° (Found: N, 8·8; As, 23·0. $C_{12}H_9O_4N_2As$ requires N, 8·7; As, 23·4%). It was insoluble in water and most organic solvents, but dissolved in aqueous sodium hydroxide, and from a strong solution of the latter the sodium salt (brown) crystallised.

10-*Bromo*-3(or 1)-*nitro*-5:10-*dihydrophenarsazine* was prepared by reducing 3(or 1)-nitrophenarsazinic acid in the presence of hydrobromic acid in the usual way. When recrystallised from benzene, it was obtained in short, reddish-brown needles, m. p. 234° (decomp.) (Found: Br, 22·15. $C_{12}H_8O_2N_2BrAs$ requires Br, 21·8%).

4-*Nitrodiphenylamine*-6'-*arsinic acid* (IX) was prepared from *p*-bromonitrobenzene (52·2 g.) and *o*-aminophenylarsinic acid (50·3 g.) in a similar manner to the isomeric compounds, the boiling, however, being continued in this case for 7½ hours. The crude product (35 g.) was recrystallised from dilute acetic acid, and the pure acid obtained as a pale yellow, microcrystalline substance, m. p. 223° (decomp.) (Found: N, 8·3. $C_{12}H_{11}O_5N_2As$ requires N, 8·3%). The alkali salts are deep orange-red in aqueous solution.

10-*Chloro*-2-*nitro*-5 : 10-*dihydrophenarsazine* (XVIII) was prepared from the preceding compound (8 g.) by reduction in the presence of hydrochloric acid in the usual way. The product (6·1 g.) was recrystallised from glacial acetic acid, in which it was somewhat sparingly soluble. It seems to be dimorphous, for it separated first in soft, yellow needles which, on standing or when the solution was stirred, changed into compact, small, orange-yellow, prismatic needles. On heating, the substance turned dark red at about 194—197° and had m. p. 276—278° (decomp.) (Found : Cl, 10·8; As, 22·95. $C_{12}H_8O_2N_2ClAs$ requires Cl, 11·0; As, 23·2%).

Phenarsazinic acid (20 g.) was nitrated under the conditions described by Burton and Gibson (J., 1926, 2244), and the nitro-acid purified as described through the sodium and barium salts. This acid, on reduction in the usual way in the presence of hydrochloric acid, gave a chloro-compound which was identical in every way with the above compound. It was obtained in soft, yellow needles which were converted into the compact, orange-yellow prisms; on heating, the behaviour was the same as that already described (Found : As, 23·05. Calc. : As, 23·2%). It must have been formed from 2-nitrophenarsazinic acid.

Phenarsazinic acid (10 g.) was nitrated as far as possible under the conditions described by Wieland and Rheinheimer (*loc. cit.*). The mixture was kept for 1½ hours after the addition of the nitric acid (*d* 1·5) was completed. The nitro-acid obtained from the sodium salt was recrystallised twice from 50% acetic acid and was then dark yellow to orange. It was reduced in the presence of hydrochloric acid in the usual way, and the product had a very indefinite melting point, melting and decomposition not being complete at 250°. After this had been further recrystallised from glacial acetic acid, it melted at 265—267° (decomp.), and although even then it was not quite pure, its behaviour when admixed with pure 10-chloro-2-nitro-5 : 10-dihydrophenarsazine showed that it was chiefly composed of this substance.

We are therefore justified in concluding that the most easily isolated product of the nitration of phenarsazinic acid is 2-nitrophenarsazinic acid, and not 4-nitrophenarsazinic acid as stated by Wieland and Rheinheimer.

10-Chloro-5 : 10-dihydrophenarsazine was also nitrated under the conditions described by Wieland and Rheinheimer. The mononitro-derivative obtained in the larger amount (for which they quoted no melting point) was oxidised by means of hydrogen peroxide (20 vol.) in glacial acetic acid solution. The product was recrystallised from glacial acetic acid and then reduced in the presence of hydrochloric acid in the usual way, being thus con-

verted into 10-chloro-2-nitro-5 : 10-dihydrophenarsazine, m. p. 276° (decomp.), identical with the product described above.

The various nitro-derivatives of 10-chloro-5 : 10-dihydrophenarsazine can be readily distinguished from 2-nitrodiphenylamine-6′-arsinic acid, since the latter dissolves in concentrated sulphuric acid to form a characteristic deep red solution, whilst the former compounds yield deep violet solutions. All the solutions change to an olive-green colour on addition of a drop of concentrated nitric acid.

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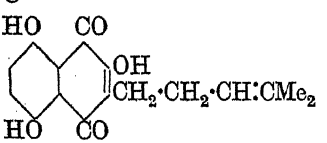
[*Received, August 26th*, 1927.]

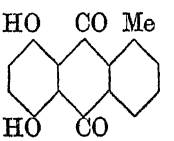
CCCXXXVI.—*A New Isomerism of Halogenohydroxybenzoyltoluic Acids.*

By MOSUKE HAYASHI.

THE roots of *Lithospermum Erythrorhizon*, commonly known as Shikon, were used in ancient Japan as an important violet dye. A few years ago the main constituent of this colouring matter was isolated by Majima and Kuroda (*Acta Phytochim.*, 1922, **1**, 43) and found to be a monoacetyl compound of a hydroxynaphthaquinone derivative. This derivative, which has been termed *shikonin* from the Japanese name of the plant, melts at 147° and has the molecular formula $C_{16}H_{16}O_5$; its constitutional formula, representing it as 2 : 5 : 8-trihydroxy-3-δ-methyl-Δ$^{\gamma}$-pentenyl-1 : 4-naphthaquinone (I), was deduced from the results of careful investigations.

(I.)



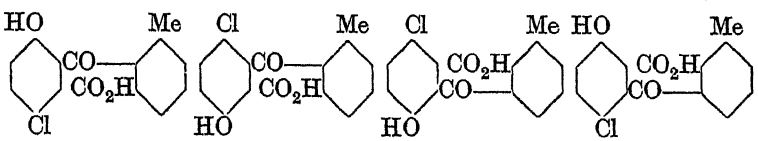


(II.)

One of the most characteristic properties of shikonin is the formation of a red sublimate on heating; this decomposition product, termed *shikizarin*, m. p. 232°, has the molecular formula $C_{15}H_{10}O_4$. Whereas shikonin itself, as a naphthaquinone derivative, is relatively unstable, shikizarin is stable enough to be regarded as an anthraquinone derivative; it gives 3-methylphthalic anhydride on oxidation with potassium permanganate. From these results, shikizarin (II) seems to be 8-methylquinizarin, formed by the extrusion of a molecule of hydrogen and of the elements of methyl alcohol from shikonin.

To decide the constitution of shikizarin, 8-methylquinizarin was synthesised by Majima by condensing 3-methylphthalic anhydride with quinol dimethyl ether and heating the dihydroxybenzoyltoluic acid thus formed with concentrated sulphuric acid.* It was identical with shikizarin, and strong support was thus obtained for the constitution of shikonin. The yield of the dihydroxybenzoyltoluic acid was, however, very poor, so the synthesis was attempted in another way by Sakurai in the same laboratory, but without much improvement in the result.* Yet another synthesis was carried out by the present author by condensing 3-methylphthalic anhydride with *p*-chloroanisole in acetylene tetrachloride solution in the presence of aluminium chloride (compare Ullmann and Schmidt, *Ber.*, 1919, **52**, 2098). Thereby chlorohydroxybenzoyltoluic acid was obtained in good yield, the methoxyl group being hydrolysed at the same time. 8-Methylquinizarin was then produced by treating this intermediate substance with concentrated sulphuric acid and heating the chlorohydroxymethylanthraquinone thus formed with a solution of boric acid in sulphuric acid. The yield was about 50% of the chlorohydroxymethylanthraquinone.

The stage of the reaction resulting in the formation of chlorohydroxymethylanthraquinone was, however, not at all simple and the action of concentrated sulphuric acid on the chlorohydroxybenzoyltoluic acid gave rise, in addition to chlorohydroxymethylanthraquinone, to an interesting isomeric change, which has been studied in some detail. The above-mentioned chlorohydroxybenzoyltoluic acid, m. p. 238—239°, may have one of the formulæ III, IV, V, and VI. Many authors (Nourrisson, *Ber.*, 1886, **19**,



(III.) (IV.) (V.) (VI.)

2103; Logodzinski, *Ber.*, 1895, **28**, 116; *Annalen*, 1905, **342**, 90; Bistrzycki and Schepper, *Ber.*, 1898, **31**, 2790; Ullmann and Schmidt, *Ber.*, 1919, **52**, 2098; Simonsen and Rau, J., 1921, **119**, 1339; Simonsen, J., 1924, **125**, 721; Eder and his co-workers, *Helv. Chim. Acta*, 1922, **5**, 3; 1923, **6**, 419, 966; 1925, **8**, 126; Bistrzycki and Krauer, *Helv. Chim. Acta*, 1923, **6**, 750; Adams and his collaborators, *J. Amer. Chem. Soc.*, 1923, **45**, 2439, 2455; 1925, **47**, 283; compare also Bentley, Gardner, and Weizmann, J., 1907, **91**, 1626) have shown that phthalic anhydride and its derivatives condense with phenolic ethers in the *p*-position to the alkyloxy-

* The details of these experiments have not yet been published.

group, provided that position is open, and with phenols in the *o*-position to the hydroxy-group, and that no condensation in the *m*-position to the alkyloxy- or hydroxy-group can be effected. The constitutional formula of the chlorohydroxybenzoyltoluic acid may therefore be either (III) or (V). As α-substituted phthalic anhydrides usually condense with phenol and its ethers through the carbonyl group adjacent to the substituent (Bistrzycki and Schepper; Simonsen and Rau; Simonsen; Eder and his co-workers; Bistrzycki and Krauer; Adams and his collaborators; *locc. cit.*), it is highly probable that the chlorohydroxybenzoyltoluic acid is 5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid (III).

By the action of concentrated sulphuric acid (98·25%) on the chlorohydroxybenzoyltoluic acid, an anthraquinone derivative, m. p. 223—224°, was obtained, and this should be 5-chloro-8-hydroxy-1-methylanthraquinone.

When 5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid was treated with concentrated sulphuric acid on the steam-bath, the greater part of the product was soluble in aqueous sodium carbonate. Two isomeric substances, differing in solubility, crystalline form, and in the amount of water of crystallisation of their salts, were obtained by fractional crystallisation of the recovered acids from alcohol; one melted at 171—171·5° and the other at 238—239°. The latter was proved to be identical with the initial substance by the mixed melting point method. These two isomerides are designated α- and β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid, respectively.

After the isolation of the α- and β-acids from the material soluble in sodium carbonate, the residue (C) melted at about 160—165° and was difficult to purify by further fractional crystallisation.

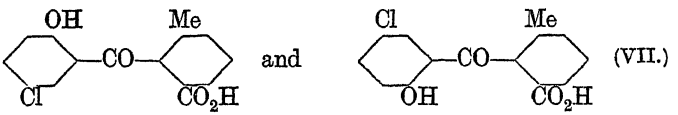
The α-acid (m. p. 171—171·5°) was treated with concentrated sulphuric acid, and the isolation of the products carried out, as in the case of the β-acid; the anthraquinone derivative, the β-acid, unchanged α-acid, and the residue (C′), from which it was difficult to separate the α- and β-acids by further fractional crystallisation, were then obtained.

When treated with concentrated sulphuric acid on the steam-bath, the residue C or C′ gave essentially the same results as those obtained from the α- or the β-acid. Therefore the residues C and C′ seem to consist of somewhat impure mixtures of the α- and β-acids, and the percentages of these acids in them can be approximately deduced from a table of melting points of mixtures of the two acids.

On treating the α-acid, the β-acid, the residue C and the residue C′ separately with concentrated sulphuric acid at room temperature, the anthraquinone derivative was not obtained, but in each case

the α- and β-acids could be isolated. Consequently the production of the anthraquinone derivative from the α- or the β-acid is preceded by a reversible change between these acids.

The α- and the β-acid, being so readily interconvertible on treatment with concentrated sulphuric acid, are probably stereoisomeric, and this view is supported by the great similarity of their ultra-violet absorption curves. This theory of the isomerism may be illustrated by the following formulæ :



(VII.)

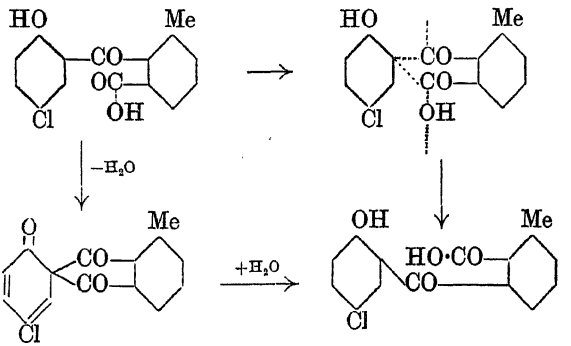
At present there is no diagnostic reaction which will enable us to apportion these configurations, but since in an equilibrium mixture of the two acids at about 100° the amount of the β-acid is very small and that of the α-acid is great, whilst the yield of the anthraquinone derivative is relatively small, it seems probable that the configuration (VII) is that of the α-acid.

The Kaufler diphenyl configuration (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250) has been employed by Cain and his collaborators (J., 1914, **105**, 1437, 1442, etc.), by Turner (J., 1915, **107**, 1495), by Kenner and his co-workers (J., 1922, **121**, 614; 1923, **123**, 779, 1043, 1948), by Brady and McHugh (J., 1923, **123**, 2047), by Bullock and Wilson (*J. Amer. Chem. Soc.*, 1923, **45**, 521), and by many other chemists to account for the stereoisomerism of diphenyl derivatives.* Moreover, Kaufler and Basel (*Ber.*, 1907, **40**, 3253) and Kenner (J., 1922, **121**, 614) expected the existence of stereoisomerides of the same kind in derivatives of diphenylmethane and diphenylethane, but so far as the author is aware, their existence has not been reported. In the case of 5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid, the author obtained results similar to those described above in connexion with the chloro-derivatives.

When 5′-chloro-2′-hydroxy-*o*-benzoylbenzoic acid, obtained by condensing phthalic anhydride with *p*-chloroanisole or *p*-chlorophenol, was heated with concentrated sulphuric acid (98·25%) on the steam-bath, 4-chloro-1-hydroxyanthraquinone was easily obtained in 90% yield (compare Ullmann, D.R.-P. 282,493), but interaction over-night at room temperature gave only a 5% yield

* More recent investigations have shown that the conception is not even necessary for the satisfactory explanation of the chemistry of the diphenyl group, and as a result of these developments in the period following the writing of this communication the author feels that the alternative structural explanation of his results requires all the more careful consideration.

of the anthraquinone, 92% of the original substance being recovered. In these experiments, two isomerides of 5′-chloro-2′-hydroxy-*o*-benzoylbenzoic acid, anticipated from the analogy with the above-mentioned benzoyltoluic acids, were not encountered. This circumstance lends some colour to the view that the isomerism of these substituted benzoylbenzoic acids is, after all, structural in accordance with one of the schemes :



Obviously, in this case the shikizarin ultimately obtained would be a homogeneous product, whereas the chlorohydroxymethylanthraquinone might consist of two isomerides. Experience in the anthraquinone group suggests that such a mixture might simulate the behaviour of a pure substance.

The investigation of the analogous isomerism of other derivatives of benzoylbenzoic acid is in progress with the object of deciding between the two possible interpretations of the results.

Experimental.

β-5′-*Chloro*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid*.—3-Methylphthalic anhydride (10 g., m. p. 115·5—116·5°) was dissolved in acetylene tetrachloride (50 c.c.), mixed with *p*-chloroanisole (10 g.), and finely powdered aluminium chloride (25 g.) gradually added in the course of 1—1½ hours, with frequent shaking, the temperature being maintained at 115—120° (oil-bath) during the addition and thereafter at 120—130° for 3 hours. The product was cooled, mixed with ice-water and, after the addition of an excess of hydrochloric acid, distilled in steam in order to remove *p*-chloroanisole and acetylene tetrachloride. The solid residue was extracted several times with boiling ammonia solution,* and the ammoniacal extracts

* Chlorohydroxymethylanthraquinone (7% of the theoretical) was isolated from the part insoluble in ammonia, and proved to be identical with the anthraquinone derivative, which was obtained from the α- or β-5′-chloro-2′-hydroxybenzoyltoluic acid, by the method of mixed melting points.

were freed from ammonia and cooled; the resinous substance that separated was removed. On acidification of the filtrate, impure β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid, m. p. about 210—220°, separated in 75% yield. The acid was redissolved in caustic alkali or in ammonia and the solution was boiled with animal charcoal, filtered, and acidified with hydrochloric acid; the almost colourless material thus precipitated was washed with water and crystallised from alcohol or glacial acetic acid (Found: C, 61·7; H, 4·0; Cl, 12·4; *M*, in camphor by Rast's method, 285. $C_{15}H_{11}O_4Cl$ requires C, 62·0; H, 3·8; Cl, 12·2%; *M*, 291). This acid melts at 238—239°, and dissolves readily in hot alcohol or glacial acetic acid, but is sparingly soluble in the cold solvents. It is easily soluble in acetone, slightly soluble in benzene, carbon tetrachloride, carbon disulphide or chloroform, and very sparingly soluble in light petroleum or water. The yellow solution in concentrated sulphuric acid develops a deep red colour. The crystalline form: rhombic system, ∝ P (from alcohol). The ultra-violet absorption curve of this acid, determined with a Hilger quartz spectrograph, shows two bands with heads at λ 3350 and 2860 Å.U.

In an experiment similar to that described above but starting from 3-methylphthalic anhydride (10 parts) and *p*-chlorophenol (9 parts), a substance, m. p. 215—225°, was isolated in 70% yield. (Chlorohydroxymethylanthraquinone, 7% of the theoretical quantity, was also isolated from the part insoluble in ammonia.) This was purified and identified as β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid, since its m. p. was not depressed on admixture with the β-acid.

The *sodium* and *barium* salts were prepared by neutralising hot alcoholic solutions of the acid with solutions of the corresponding bases, and recrystallised from water by cooling their solutions with ice. The specimens were kept in a balance room until the weight was constant for a few hours [Found for the sodium salt (temperature of the room, 12°; relative humidity, 85%): loss at 105°/10 mm., 25·6; Na, 5·4. $C_{15}H_{10}O_4ClNa,6H_2O$ requires H_2O, 25·7; Na, 5·5%. Found for the barium salt (temperature of the room, 11°; relative humidity, 84%): loss at 105°/10 mm., 16·6; Ba, 15·7. $(C_{15}H_{10}O_4Cl)_2Ba,8H_2O$ requires H_2O, 16·7; Ba, 16·0%]. On standing in the atmosphere, the water of crystallisation was gradually lost, the more quickly the higher the room temperature. The sodium salt is readily soluble and the barium salt moderately easily soluble in water.

α-*5′-Chloro-2′-hydroxy-2-benzoyl*-m-*toluic Acid.*—The β-acid (1 g.) was heated with sulphuric acid (6 c.c.; 98·25%) in a boiling water-bath for about 1 hour. On pouring the product into ice-water, a

dirty green, sticky precipitate separated and after warming for a few minutes this was collected, washed with water by decantation, and stirred with an excess of dilute aqueous sodium carbonate; a yellow substance (20—25% yield), m. p. 220—222°, remained undissolved. This substance was recrystallised several times from glacial acetic acid and proved to be chlorohydroxymethylanthraquinone (see p. 2524). From the yellow filtrate, acidified with hydrochloric acid, a sticky substance was precipitated which crystallised on being warmed for a few minutes or kept at the ordinary temperature for several days. The solid was collected, washed with water, and dried over sulphuric acid in a vacuum desiccator, a faintly yellow, crystalline mass being obtained (yield, 55—75%). It sintered at about 160° and melted to a clear liquid at about 170°. On fractional crystallisation from alcohol, two forms were separated. The residue (C), from which nothing definite could be isolated by further recrystallisation, melted at 160—165° (yield, 10—30% of the β-acid). The less soluble fraction (yield, about 1%), m. p. 220—235°, was recrystallised from alcohol and proved to be identical with the β-acid by the mixed melting point method. The more soluble fraction (yield, 35—50%) melted at 169—171° and was recrystallised several times from aqueous alcohol (Found: C, 61·8; H, 3·8; Cl, by Nomura and Murai's method, 11·9; *M*, in camphor by Rast's method, 287. $C_{15}H_{11}O_4Cl$ requires C, 62·0; H, 3·8; Cl, 12·2%; *M*, 291). The substance is moderately easily soluble in benzene, dissolves to some extent in water, and is readily soluble in alcohol or glacial acetic acid. It dissolves in concentrated sulphuric acid to a deep red solution, a little heat being developed. Like the β-isomeride, it is soluble in dilute aqueous caustic alkali to a yellow solution. Crystalline form: rhombic system, ∞ P, P (from a mixture of alcohol and water). This acid has two absorption bands with heads at λ 3390 and 2860.

α-5′-Chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid was treated with sulphuric acid (98·25%) under the same conditions as in the case of the β-acid, and the separation and identification of the reaction products were carried out as before. In this separation the chlorohydroxymethylanthraquinone and the β-acid, together with the initial substance, were isolated. Nothing definite could be isolated, by further recrystallisation, from the residue (C′).

However, the α- and β-acids and the chlorohydroxymethylanthraquinone were isolated from the residue (C or C′) by applying the same method as in the preceding cases, after treatment with concentrated sulphuric acid (98·25%).

In the latter three cases, the percentages of the α- and β-acids

and of the chlorohydroxymethylanthraquinone thus formed were almost the same as in the case of the β-acid. The details are given below in tabular form.

TABLE I.

Action of 98·25% Sulphuric Acid at about 95°.

Initial substance.	Insoluble in dil. Na_2CO_3 soln. (crude anthraquinone derivative). M. p.	%	Soluble in dilute sodium carbonate solution. M. p.	%		M. p.	%
β-Acid	220—222°	20—25	160—170°	55—75	Crude α-acid	169—171°	35—50
					Crude β-acid	220—235	1
					Residue (C)	160—165	10—30
α-Acid	219—222	20—25	158—170	60—70	Crude α-acid	168—170	30—50
					Crude β-acid	220—230	trace
					Residue (C′)	160—165	20—30
Residue C or C′	210—220	20—25	158—170	60—70	Crude α-acid	169—170	30—50
					Crude β-acid	220—235	
					Residue	160—165	10—30

The anthraquinone derivative was not obtained when a solution of the α- or the β-acid or of the residue (C or C′) in concentrated sulphuric acid (98·25%) was kept over-night at room temperature (see Table II). This method is preferable for the preparation of the α-acid from the β-acid.

TABLE II.

Action of 98·25% Sulphuric Acid at Room Temperature.

Initial substance.	Soluble in dilute sodium carbonate solution. M. p.	%		M. p.	%
β-Acid	168—170·5°	95—98	Crude α-acid	170—171°	70—80
			Crude β-acid	could not be separated	
			Residue (D)	163—168	15—25
α-Acid	,,	,,	Crude α-acid	169—171°	70—80
			Crude β-acid	could not be separated	
			Residue (D′)	163—168	20—25
Residue C or C′	,,	,,	Crude α-acid	169—171°	60—80
			Crude β-acid	could not be separated	
			Residue	160—166	15—20

It is clear from the data in Table III that the velocity of the reaction by which the β-acid changes to the α-acid is extremely rapid.

TABLE III.

The β-acid (0·1 g.) was treated with 98·25% sulphuric acid (1 c.c.) at 24° for the times stated.

Time (mins.).	Reaction product, m. p.	% α-Acid (from Table IV).	Time (mins.).	Reaction product, m. p.	% α-Acid (from Table IV).
5	162·5—169°	75—80	21	165·5—168·5°	*ca.* 93
10	162·5—165	*ca.* 80	30	165·5—169	*ca.* 95
16	162 —166	*ca.* 85	60	168·5—170·5	*ca.* 98

TABLE IV.

Melting Points of Mixtures of the α- and β-Acids.

β-Acid %.	α-Acid %.	M. p.	β-Acid %.	α-Acid %.	M. p.
0·0	100·0	171—171·5°	18·7	81·3	162—165°
1·3	98·7	169—171	19·2	80·8	162—166
2·4	97·6	168—170	24·2	75·8	162—200
3·6	96·4	166—170	29·2	70·8	162—205
9·5	90·5	163—167	40·4	59·6	162—215
13·4	86·6	163—167	49·5	50·5	162—220

The *sodium* and *barium* salts of the α-acid were prepared and analysed under conditions similar to those described for the sodium and barium salts of the β-acid. The *sodium* salt is readily soluble in water and closely resembles the sodium salt of the β-acid (Found: loss at 105°/10 mm., 19·0; Na, 5·9. $C_{15}H_{10}O_4ClNa,4H_2O$ requires H_2O, 18·7; Na, 6·0%). The *barium* salt is moderately easily soluble in water and does not effloresce at about 12° [Found: loss at 105°/10 mm., 4·7; Ba, 18·4. $(C_{15}H_{10}O_4Cl)_2Ba,2H_2O$ requires H_2O, 4·8; Ba, 18·3%]. The solubility of the α-acid and its salts is generally greater than that of the β-acid and its salts.

Chlorohydroxymethylanthraquinone.—A mixture of α- or β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid (1 g.) and sulphuric acid (6 c.c.; 98·25%) was heated at 115—120° for about an hour, cooled, and added to ice-water, and the green precipitate that separated was collected and treated with an excess of dilute sodium carbonate solution. A yellow substance (yield, 65%), m. p. 220—222°, remained undissolved; after several recrystallisations from glacial acetic acid it melted at 223—224° (Found: C, 65·8; H, 3·6; Cl, 13·3. $C_{15}H_9O_3Cl$ requires C, 66·1; H, 3·3; Cl, 13·0%). This substance is easily soluble in hot benzene, appreciably soluble in hot glacial acetic acid, and sparingly soluble in hot alcohol. It dissolves with difficulty in caustic alkalis and easily in concentrated sulphuric acid, giving a red solution in each case.

5 : 8-*Dihydroxy*-1-*methylanthraquinone* (8-*Methylquinizarin*).—Chlorohydroxymethylanthraquinone (1 g.) was gradually added to a solution of boric acid (2·4 g.) in concentrated sulphuric acid (10 c.c.) at 140—150°, and the whole was heated at 150—160° until the evolution of hydrogen chloride ceased. After cooling, the product was poured into ice-water, and the reddish-black precipitate was collected, and well washed with hot water. The substance was purified by dissolution in caustic soda and reprecipitation (yield, about 50%) and then by crystallisation several times from *iso*butyl alcohol or glacial acetic acid (Found: C, 70·6; H, 4·0. Calc., C, 70·9; H, 4·0%). The dark red crystals melted at 233—234° and at the same temperature when mixed with a specimen of

8-methylquinizarin (m. p. 232—233°) obtained from shikonin by Majima and Kuroda (*loc. cit.*).

β-5′-*Bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid.*—Aluminium chloride (12·5 g.) was gradually added to a solution of 3-methylphthalic anhydride (5 g.) and *p*-bromophenol (7·5 g.) in acetylene tetrachloride (20 c.c.), and the subsequent treatment and the separation of the reaction products were carried out as in the case of the chloro-derivative. Impure β-5′-*bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic acid*, m. p. about 220—230°, was obtained in 75% yield from the part soluble in ammonia, and bromohydroxymethylanthraquinone in about 6% yield from the insoluble part. The former, after several crystallisations from alcohol, had m. p. 246—246·5° (Found: C, 53·8; H, 3·5; Br, by Nomura and Murai's method, 23·8. $C_{15}H_{11}O_4Br$ requires C, 53·7; H, 3·3; Br, 23·8%). It is easily soluble in hot alcohol, hot glacial acetic acid or hot acetone, and sparingly soluble in carbon disulphide, carbon tetrachloride or benzene. It is very sparingly soluble in water or light petroleum. The solution of this acid in concentrated sulphuric acid is at first yellow, but soon becomes deep red. The acid is also soluble in dilute caustic alkali to a yellow solution. It exhibits an absorption band with a head at λ 3335.

The bromohydroxymethylanthraquinone mentioned above was proved to be identical with bromohydroxymethylanthraquinone, which was obtained from α- or β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid, by the mixed melting point method.

α-5′-*Bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid.*—After a solution of β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid in sulphuric acid (6 c.c.; 98·25%) had been heated in the boiling water-bath for ½ hour, the reaction products were treated with an excess of dilute sodium carbonate solution, bromohydroxymethylanthraquinone, a yellow substance, m. p. 187—195°, remaining undissolved (yield, 8—10%); a crystalline mass, m. p. 157—162° (yield, 70—85%) was obtained from the yellow filtrate on acidification with hydrochloric acid. On repeated crystallisation from alcohol, two fractions were isolated. The less soluble crystals (about 1%) melted at 240—243°, and the more soluble ones (50—70%) at 161—164°. The former fraction was recrystallised from alcohol and proved to be identical with β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid by the mixed melting point method. The latter was recrystallised from aqueous alcohol (Found: C, 53·7; H, 3·5; Br, by Nomura and Murai's method, 24·1. $C_{15}H_{11}O_4Br$ requires C, 53·7; H, 3·3; Br, 23·8%). This isomeride melts at 163·5—164°, and is readily soluble in alcohol, glacial acetic acid, or acetone, moderately readily soluble in benzene, carbon disulphide, or carbon tetrachloride, and

very sparingly soluble in light petroleum or water. Its solubility is generally greater than that of the β-acid. It dissolves in concentrated sulphuric acid and in dilute aqueous caustic alkali, giving a red and a yellow solution, respectively. This acid has an absorption band with a head at λ 3345.

The α-acid was treated with sulphuric acid (98·25%) at 100°, and bromohydroxymethylanthraquinone and the α- and β-acids were then separated by applying the method used in the case of the β-acid. The same results were obtained from the residue (R or R′) (see Table V).

TABLE V.

Initial substance.	Insoluble in dil. Na_2CO_3 soln. (crude anthraquinone derivative).		Soluble in dilute sodium carbonate solution.				
	M. p.	%.	M. p.	%.		M. p.	%.
β-Acid	187—195°	8—10	157—162°	70—85	Crude α-acid	161—164°	50—70
					Crude β-acid	240—243	1
					Residue (R)	158—161	10—25
α-Acid	188—194	5—10	159—162	70—85	Crude α-acid	163—164	50—70
					Crude β-acid	very small	
					Residue (R′)	158—161	10—25
Residue R or R′	187—195	5—10	158—161	70—85	Crude α-acid	163—164	40—70
					Crude β-acid	240—245	1
					Residue	158—161	10—30

The Sodium and Potassium Salts of α- *and* β-5′-*Bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acids*.—These salts were prepared by neutralising hot alcoholic solutions of the acids with solutions of the corresponding alkali hydroxides, and recrystallised from water by cooling in ice. After standing in a balance room until the weight was constant for a few hours, they were analysed (Temp. of room, 6°; relative humidity, 87%. Found for sodium salts of α-acid and of β-acid, respectively: loss at 105°/10 mm., 17·0 and 23·5; Na, 5·4 and 5·0. $C_{15}H_{10}O_4BrNa,4H_2O$ and $C_{15}H_{10}O_4BrNa,6H_2O$ respectively require H_2O, 16·8 and 23·2; Na, 5·4 and 4·9%. Temp. of room, 11°; relative humidity, 83%. Found for potassium salts of α-acid and of β-acid, respectively: loss at 105°/10 mm., 4·3 and 12·4; K, 9·8 and 9·1. $C_{15}H_{10}O_4BrK,H_2O$ and $C_{15}H_{10}O_4BrK,3H_2O$ respectively require H_2O, 4·6 and 12·7; K, 10·0 and 9·2%). The two sodium salts and the β-potassium salt gradually lost their water of crystallisation in the air.

Bromohydroxymethylanthraquinone.—The above-mentioned anthraquinone derivatives obtained from α- and β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acids and the residues (R and R′) crystallised separately from *iso*butyl alcohol in yellow crystals, m. p. 198—198·5°, and were proved to be identical with each other by the mixed melting point method (Found: C, 56·7; H, 3·0; Br, by Nomura and Murai's method, 25·15. $C_{15}H_9O_3Br$ requires C, 56·8; H, 2·9; Br, 25·2%). This bromohydroxymethylanthraquinone is

easily soluble in benzene, glacial acetic acid, *iso*butyl alcohol, carbon disulphide, carbon tetrachloride, and acetone when the solvents are hot. It is moderately readily soluble in alcohol and sparingly soluble in light petroleum. It dissolves to a slight extent in dilute aqueous caustic alkali and easily in concentrated sulphuric acid, giving red solutions.

In conclusion, the author wishes to express his gratitude to Professor Rikô Majima, at whose suggestion this investigation was made, for his advice and helpful criticism, to Dr. Hiroshi Nomura for the micro-analyses, to Saichirô Nagami Rg. s. for the spectrographic investigation, and to Kenjirô Katô Rg. s. for the crystallographic measurements.

TÔHOKU IMPERIAL UNIVERSITY,
SENDAI, JAPAN.

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CCCXXXVII.—*Reactions of Thiosemicarbazones. Part III.*

By WILLIAM BAIRD, ROBERT BURNS, and FORSYTH JAMES WILSON.

IT has been found that the sodium derivative of acetonethiosemicarbazone reacts with ethyl, propyl, allyl, and butyl halides, also with ethyl ω-bromo-*o*-toluate, to give *S*-alkyl compounds of the type $CMe_2{:}N{\cdot}N{:}C(SR){\cdot}NH_2$. Whilst *S*-benzylthiosemicarbazide (J., 1922, **121**, 870) gave a monohydrochloride only and the benzylidene derivative was non-basic, the *S*-alkylthiosemicarbazides described in this paper are diacid bases giving dihydrochlorides of the type $NH_2{\cdot}N{:}C(SR){\cdot}NH_2,2HCl$, which were obtained from the parent compounds by hydrolysis with acid. The benzylidene derivatives are monoacid bases and were obtained as monohydrochlorides, $CHPh{:}N{\cdot}N{:}C(SR){\cdot}NH_2,HCl$. These acetone- and benzaldehyde-*S*-alkylthiosemicarbazones melt at much lower temperatures than the thiosemicarbazones themselves and it therefore appears probable that the thiosemicarbazones contain the group $-C{:}S$ and not $-C{\cdot}SH$.

Whilst the sodium derivative of acetonethiosemicarbazone reacts with esters of α-halogenated monobasic acids to produce cyclic compounds (J., 1923, **123**, 799), esters of β- and γ-halogenated monobasic acids behave quite differently. With ethyl β-chloro-*n*-butyrate and ethyl β-bromo-β-phenylpropionate, elimination of hydrogen halide as sodium halide occurred with formation of acetonethiosemicarbazone and the unsaturated ester, ethyl croton-

ate and ethyl cinnamate, respectively: ethyl γ-chloro-*n*-butyrate, ethyl γ-chloro-*n*-valerate, and ethyl γ-chloro*iso*hexoate reacted in a similar way. These reactions were carried out in alcoholic solution; in benzene suspension, no reaction took place even after several hours' boiling.

The interaction of thiosemicarbazones and primary amines, when hot, takes place according to the scheme $CRR':N\cdot NH\cdot CS\cdot NH_2 + R''NH_2 = CRR':N\cdot NH\cdot CS\cdot NHR'' + NH_3$, yielding δ-substituted thiosemicarbazones with the alkyl or aryl group attached, not to sulphur as in the preceding cases, but to nitrogen. The reaction is similar to that between semicarbazones and primary amines investigated by Borsche and others (*Ber.*, 1901, **34**, 4299; 1904, **37**, 3177; 1905, **38**, 83) and by workers in these laboratories; thiosemicarbazones, however, react much more slowly. Acetonethiosemicarbazone was chiefly employed, the amines being benzylamine, α-phenylethylamine, aniline, β-naphthylamine, and *n*-heptylamine. These δ-substituted thiosemicarbazones on hydrolysis with dilute hydrochloric acid yielded the corresponding thiosemicarbazide hydrochlorides, $NH_2\cdot NH\cdot CS\cdot NHR'',HCl$, with the exception of the β-naphthyl derivative, which suffered further decomposition; from these hydrochlorides the thiosemicarbazides were obtained. That these compounds contain the substituent in the δ-position is evident from the fact that acetonethiosemicarbazone and aniline yielded a product identical with a specimen of acetone-δ-phenylthiosemicarbazone prepared in the usual way; also δ-benzylthiosemicarbazide, synthesised from benzylthiocarbimide and hydrazine hydrate, $CH_2Ph\cdot NCS + NH_2\cdot NH_2 = CH_2Ph\cdot NH\cdot CS\cdot NH\cdot NH_2$ (a general reaction for the preparation of such substances), was identical with the compound obtained by us.

It is hoped to prepare the optically active δ-α-phenylethylthiosemicarbazides and to investigate possible applications of these compounds.

EXPERIMENTAL.

The Reaction between the Sodium Derivative of Acetonethiosemicarbazone and Alkyl Halides.—Procedure. Alcoholic solutions of acetonethiosemicarbazone and sodium ethoxide (equimolecular quantities) were mixed, boiled for 10 minutes, and cooled, the alkyl halide (1 mol.) was then added, and after 12 hours the mixture was heated under reflux for 15 minutes. The solution was then evaporated to dryness under reduced pressure and the acetone-*S*-alkylthiosemicarbazone was separated from the sodium halide and acetonethiosemicarbazone by dissolving it in ether; after evaporation of the ether, it was recrystallised from light petroleum. These compounds were readily soluble in the usual organic solvents.

Hydrolysis was effected by boiling under reflux for 15 minutes with 0·5*N*-hydrochloric acid; unchanged substance and any mercaptan formed were then removed by extraction with ether, the acid solution was concentrated under reduced pressure, and the *S*-alkylthiosemicarbazide dihydrochloride obtained in the solid form by keeping the residual syrup over sulphuric acid or phosphorus pentoxide in an evacuated desiccator. These dihydrochlorides were very hygroscopic and very soluble in water.

The benzylidene monohydrochloride was obtained by shaking an aqueous solution of the dihydrochloride with a little benzaldehyde, washing the product with a little ether, and then precipitating it from alcoholic solution by addition of ether. These compounds were readily soluble in alcohol and sparingly soluble or insoluble in benzene, ether, and water. The benzylidene derivative itself was obtained by treating the monohydrochloride with the necessary quantity of sodium carbonate in aqueous-alcoholic solution, evaporating the solution to dryness under reduced pressure, extracting the residue with ether, and, after evaporation of the ether, recrystallising the product from light petroleum. These derivatives were soluble in the usual organic solvents.

With ethyl bromide. *Acetone*-S-*ethylthiosemicarbazone* formed flat, transparent prisms, m. p. 55°, having a slight, unpleasant odour (yield, 65—70%) (Found: N, 26·4. $C_6H_{13}N_3S$ requires N, 26·4%). S-*Ethylthiosemicarbazide dihydrochloride* was obtained as a white powder after being kept for several weeks over phosphorus pentoxide; it melted indefinitely at about 60° (Found: HCl, 37·7. $C_3H_9N_3S,2HCl$ requires HCl, 38·0%). *Benzaldehyde*-S-*ethylthiosemicarbazone hydrochloride* formed fine, colourless needles, m. p. 195° (Found: N, 17·2. $C_{10}H_{13}N_3S,HCl$ requires N, 17·2%); *benzaldehyde*-S-*ethylthiosemicarbazone* formed flat prisms, m. p. 66° (Found: N, 20·2. $C_{10}H_{13}N_3S$ requires N, 20·3%).

With propyl bromide. *Acetone*-S-*propylthiosemicarbazone* distilled at 121°/7 mm.; the distillate solidified on cooling in carbon dioxide and ether and then melted at 26—27° (Found: N, 24·2. $C_7H_{15}N_3S$ requires N, 24·3%). S-*Propylthiosemicarbazide dihydrochloride* was a thick syrup which would not solidify (Found: HCl, 35·3. $C_4H_{11}N_3S,2HCl$ requires HCl, 35·4%). *Benzaldehyde*-S-*propylthiosemicarbazone hydrochloride* formed lustrous needles, m. p. 209° (Found: N, 16·3. $C_{11}H_{15}N_3S,HCl$ requires N, 16·3%); *benzaldehyde*-S-*propylthiosemicarbazone* formed short prisms, m. p. 54° (Found: N, 18·9. $C_{11}H_{15}N_3S$ requires N, 19·0%).

With allyl iodide. *Acetone*-S-*allylthiosemicarbazone* crystallised in flat, transparent prisms (yield, 75%), m. p. 51° (Found: N, 24·5. $C_7H_{13}N_3S$ requires N, 24·6%). S-*Allylthiosemicarbazide di-*

hydrochloride, a crystalline mass, melted at 75° (Found : HCl, 35·4. $C_4H_9N_3S,2HCl$ requires HCl, 35·9%). *Benzaldehyde*-S-*allylthiosemicarbazone hydrochloride* formed lustrous plates, m. p. 190° (Found : HCl, 14·2; N, 16·2. $C_{11}H_{13}N_3S,HCl$ requires HCl, 14·3; N, 16·4%); *benzaldehyde*-S-*allylthiosemicarbazone* formed transparent, rhombic prisms, m. p. 42° (Found : N, 19·0. $C_{11}H_{13}N_3S$ requires N, 19·2%).

With n-*butyl bromide*. *Acetone*-S-*butylthiosemicarbazone*, a colourless oil of b. p. 146°/16 mm., did not solidify when strongly cooled and became slightly coloured on standing (Found : N, 22·4. $C_8H_{17}N_3S$ requires N, 22·5%). S-*Butylthiosemicarbazide dihydrochloride* formed a crystalline mass, m. p. 100—101° (decomp.) (Found : HCl, 33·1; N, 19·1. $C_5H_{13}N_3S,2HCl$ requires HCl, 33·2; N, 19·1%). *Benzaldehyde*-S-*butylthiosemicarbazone* was obtained as a viscid oil which solidified on cooling in ether and carbon dioxide; the solid, after being pressed on porous tile, crystallised from light petroleum in transparent prisms, m. p. 50° (Found : N, 17·8. $C_{12}H_{17}N_3S$ requires N, 17·9%).

With ethyl ω-*bromo*-o-*toluate*. *Acetone*-S-o-*carbethoxybenzylthiosemicarbazone*, $CMe_2{:}N{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2Et){\cdot}NH_2$, formed pale yellow, transparent prisms, m. p. 66°, from light petroleum containing a little benzene; yield, 70% (Found : N, 14·3. $C_{14}H_{19}O_2N_3S$ requires N, 14·3%). S-o-*Carbethoxybenzylthiosemicarbazide dihydrochloride*, $NH_2{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2Et){\cdot}NH_2,2HCl$, a crystalline mass, melted at 125—130° (decomp.) (Found : HCl, 22·2; N, 12·7. $C_{11}H_{15}O_2N_3S,2HCl$ requires HCl, 22·4; N, 12·9%). *Benzaldehyde*-S-o-*carbethoxybenzylthiosemicarbazone hydrochloride* formed lustrous, white plates, m. p. 115°, containing $1H_2O$ (Found : HCl, 8·7; N, 10·5. $C_{18}H_{19}O_2N_3S,HCl,H_2O$ requires HCl, 9·2; N, 10·6%); *benzaldehyde*-S-o-*carbethoxybenzylthiosemicarbazone* crystallised from light petroleum, containing a little benzene, in short, transparent prisms, m. p. 74° (Found : N, 12·2. $C_{18}H_{19}O_2N_3S$ requires N, 12·3%).

Interaction of Thiosemicarbazones and Primary Amines when Hot.—Procedure. With one exception (acetophenonethiosemicarbazone, as noted below), acetonethiosemicarbazone was used throughout. Equimolecular quantities of the reactants were heated under reflux in toluene solution or suspension at 125—130° until evolution of ammonia ceased; if necessary, the solution was then evaporated under reduced pressure. Hydrolysis was effected by refluxing with 6% hydrochloric acid, followed, if necessary, by evaporation under reduced pressure.

With benzylamine (20 hours). On cooling, *acetone*-δ-*benzylthiosemicarbazone* and a little unchanged substance separated. The product was crystallised from alcohol (prismatic needles) and then from benzene (plates); it melted at 147—148°, had a slightly

creamy tint, and was insoluble in ether and light petroleum (yield, 65%) (Found: N, 18·9; S, 14·4. $C_{11}H_{15}N_3S$ requires N, 19·0; S, 14·5%). After hydrolysis (1 g.; 20 c.c. of acid; 20 minutes) the solution, which contained acetone as shown by distillation, was filtered from a small amount of insoluble matter and evaporated after removal of the crystals which separated on cooling. The residue and the crystals were united and extracted with absolute alcohol to remove hydrazine hydrochloride; the alcoholic extract on cooling deposited *δ-benzylthiosemicarbazide hydrochloride* in colourless plates, of m. p. 189° (decomp.) after recrystallisation (yield, 87%). It was insoluble in ether and benzene, but soluble in warm water (Found: Cl, 16·2. $C_8H_{11}N_3S,HCl$ requires Cl, 16·3%). The formation of hydrazine hydrochloride and an odour of cress (due probably to thiocarbimide) after the hydrolysis showed that some decomposition had occurred. *δ-Benzylthiosemicarbazide* was obtained by boiling 0·8 g. of the hydrochloride with 20 c.c. of water for 5 minutes (an odour of thiocarbimide was apparent); the base deposited on cooling was recrystallised from absolute alcohol and then from benzene. It formed glistening leaves (yield, 76%), m. p. 130°, insoluble in light petroleum and slightly soluble in ether and water. The aqueous solution gave a white precipitate with silver nitrate (Found: N, 23·2. $C_8H_{11}N_3S$ requires N, 23·2%). The *benzylidene* derivative, prepared from benzaldehyde and the base or the hydrochloride in aqueous-alcoholic solution, crystallised from light petroleum–alcohol in long, matted needles, m. p. 133—134° (Found: N, 15·7. $C_{15}H_{15}N_3S$ requires N, 15·6%). δ-Benzylthiosemicarbazide, identical with the specimen just described (mixed m. p. test), was prepared in good yield by mixing equimolecular quantities of benzylthiocarbimide and hydrazine hydrate in ice-cold alcoholic solution. Heat was developed and the substance, which soon separated, was recrystallised from alcohol (tabular prisms) and then from benzene (leaves); both forms melted at 130°.

Acetophenonethiosemicarbazone and benzylamine reacted much more slowly (42 hours). *Acetophenone-δ-benzylthiosemicarbazone*, which separated on cooling (a little more was obtained by evaporation), crystallised from benzene as a mass of fine, colourless needles, m. p. 157—159°, and from alcohol in colourless plates, m. p. 160—161° (yield, 85%) (Found: N, 14·9; S, 11·2. $C_{16}H_{17}N_3S$ requires N, 14·8; S, 11·3%). The hydrolysis (1 g.; 20 c.c. of acid; 4½ hours), which was slow and incomplete, gave acetophenone and δ-benzylthiosemicarbazide hydrochloride besides hydrazine hydrochloride and benzylthiocarbimide.

With α-phenylethylamine (35½ hours). The solution after filtration

from a small quantity of insoluble matter and evaporation left a viscid oil which set to a transparent resin on cooling. The solution of this in a little hot absolute alcohol deposited crystals of *acetone-δ-α-phenylethylthiosemicarbazone* after cooling and scratching; recrystallisation from alcohol gave colourless, tabular prisms, m. p. 89—90° (yield, 66%) (Found: N, 18·0; S, 13·8. $C_{12}H_{17}N_3S$ requires N, 17·9; S, 13·6%). The substance was fairly soluble in benzene, sparingly soluble in light petroleum, and could be crystallised from a mixture of these solvents. The solution obtained by hydrolysis (1 g.; 20 c.c. of acid; 17 minutes) contained acetone and had an odour of thiocarbimide; a small quantity of an oil which was deposited on cooling was removed. The residue obtained by evaporation of the solution was dissolved in hot alcohol–benzene, and concentration in a vacuum then gave small, colourless plates of *δ-α-phenylethylthiosemicarbazide hydrochloride*, m. p. 157—158° (yield, 80%) (Found: Cl, 15·5. $C_9H_{13}N_3S,HCl$ requires Cl, 15·3%). The *benzylidene* derivative, prepared in the usual way, tended to separate as an oil but formed colourless plates, m. p. 128—129°, from light petroleum (Found: N, 15·0. $C_{16}H_{17}N_3S$ requires N, 14·8%). An aqueous solution of the hydrochloride was boiled with barium carbonate, and the residue obtained by evaporation of the filtrate under reduced pressure was extracted with benzene. This extract, after drying and spontaneous evaporation in a vacuum, gave an oil which solidified on standing; recrystallisation from alcohol–light petroleum gave a crystalline mass of *δ-α-phenylethylthiosemicarbazide*, m. p. 84°, which was extremely soluble in alcohol and sparingly soluble in light petroleum (Found: N, 21·6. $C_9H_{13}N_3S$ requires N, 21·5%).

With aniline (20 hours at 120—125° and 17 hours at 130—135°). Some hydrogen sulphide was evolved and a small amount of insoluble matter separated. After cooling and filtration, the toluene was evaporated, leaving a viscid oil which solidified on cooling and scratching. Recrystallisation from alcohol gave plates (yield, only 30%) of acetone-δ-phenylthiosemicarbazone, which was identified by comparison with an authentic specimen. The insoluble matter after recrystallisation from alcohol gave glistening leaves, softening at about 235° and melting at 245°. The quantity obtained was too small for identification.

With β-naphthylamine (18 hours). An appreciable quantity of an insoluble substance was formed, and hydrogen sulphide and ammonia were evolved. The substance was collected and after extraction with boiling absolute alcohol was crystallised from alcohol–pyridine. The colourless crystals softened and darkened at about 266° and melted at about 275° (Found: N, 15·5%).

This substance may be *di-β-naphthyliminotetrahydrothiodiazole* ($C_{22}H_{16}N_4S$ requires N, 15·2%) produced from acetone-δ-β-naphthylthiosemicarbazone by the reaction $2CMe_2{:}N{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7 = CMe_2{:}N{\cdot}N{:}CMe_2 + C_{10}H_7{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$, the hydrazinedithiocarbo-β-naphthylamide then giving di-β-naphthylimino-tetrahydrothiodiazole, $\begin{vmatrix} NH{\cdot}C{:}N{\cdot}C_{10}H_7 \\ NH{\cdot}C{:}N{\cdot}C_{10}H_7 \end{vmatrix} > S$, and hydrogen sulphide (compare Busch and Schmidt, *Ber.*, 1913, **46**, 2241, on the corresponding phenyl derivatives; also Pulvermacher, *Ber.*, 1894, **27**, 616). The toluene solution on cooling in ice deposited a substance which, after repeated recrystallisation from alcohol, benzene, and finally from alcohol to remove a little insoluble matter, gave yellow plates (yield, 60%) of *acetone-δ-β-naphthylthiosemicarbazone*, m. p. 150—151°; from benzene it separated apparently amorphous, m. p. 137—138° (Found: N, 16·4. $C_{14}H_{15}N_3S$ requires N, 16·3%). The substance was easily soluble in hot alcohol and hot benzene. Hydrolysis with acid gave acetone, hydrazine hydrochloride, a small amount of an unidentified hydrochloride which softened at 175° and decomposed at 190°, and also a substance insoluble in water and alcohol. The last substance separated from alcohol–pyridine as a white, apparently amorphous powder, which began to decompose at about 220° and finally melted at 252°; it became slightly pink on standing (Found: N, 13·7. $C_{22}H_{18}N_4S_2$ requires N, 13·9%). It is believed to be *hydrazinedithiocarbo-β-naphthylamide*, formed by decomposition of δ-β-naphthylthiosemicarbazide hydrochloride: $2(NH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7,HCl) =$

$$C_{10}H_7{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7 + N_2H_4,2HCl.$$

With n-*heptylamine* (21½ hours). The toluene solution on evaporation left a viscid oil which crystallised on cooling. On dissolving this in hot absolute alcohol and cooling the solution in ice, *acetone-δ-heptylthiosemicarbazone* separated, and recrystallisation from light petroleum gave silvery, glistening plates (yield, 65%), m. p. 75° (Found: N, 18·4. $C_{11}H_{23}N_3S$ requires N, 18·3%). The substance was easily soluble in benzene, ether, and carbon tetrachloride, and moderately or slightly soluble in other organic solvents. The solution obtained by hydrolysis (1 g.; 20 c.c. of acid; 10 minutes) contained acetone, and on cooling, *δ-heptylthiosemicarbazide hydrochloride* separated. This, on recrystallisation from light petroleum containing a little alcohol, formed silvery, glistening leaves, m. p. 135—136°, which were easily soluble in hot water, very soluble in alcohol, and insoluble in other common solvents (Found: N, 18·5. $C_8H_{19}N_3S,HCl$ requires N, 18·6%). The *benzylidene* derivative formed matted needles, m. p. 73°, from light petroleum (Found:

N, 15·3. $C_{15}H_{23}N_3S$ requires N, 15·2%). *δ-Heptylthiosemicarbazide*, which formed silky, glistening, acicular plates, m. p. 54—55°, was prepared by boiling the hydrochloride with sodium carbonate in aqueous-alcoholic solution; the solution was filtered from the excess of sodium carbonate and allowed to evaporate spontaneously in a vacuum; extraction of the residue with hot light petroleum and recrystallisation from the same solvent gave the desired product (Found: N, 22·3. $C_8H_{19}N_3S$ requires N, 22·2%).

In conclusion, we desire to thank the Governors of this College for Research Assistantships which have enabled two of us (W. B. and R. B.) to take part in this investigation. We wish also to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the cost of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, August 12th*, 1927.]

CCCXXXVIII.—*The Atomic Weight of Antimony from Different Sources.*

By KOLAR RAMAKRISHNAIYER KRISHNASWAMI.

THREE determinations of the atomic weight of antimony have been made during the last seven years. Willard and McAlpine (*J. Amer. Chem. Soc.*, 1921, **43**, 797) obtained the value 121·773, Weatherill (*ibid.*, 1924, **46**, 2437) 121·748, and Hönigschmid, Linhard, and Zintl (*Z. anorg. Chem.*, 1924, **136**, 257) 121·76. These figures are in good agreement, but in each case the antimony used was obtained from Kahlbaum. Muzaffar (*J. Amer. Chem. Soc.*, 1923, **45**, 2009) has, however, published results for antimony from Brazil and other sources for which he obtained values varying from 121·444 to 122·374.

In order to see if similar variations were to be found with antimony from a different part of the world, determinations have been made with four ores of Indian and Burmese origin, whilst for comparison parallel determinations have been conducted with a sample of Kahlbaum's antimony. The results agree very closely with those of the three observers mentioned above, and the variation for different ores is within the limit of experimental error.

EXPERIMENTAL.

A few trials were made of Muzaffar's method, but in spite of its apparent simplicity certain disadvantages became evident in practice, and it was abandoned. These attempts will be referred to

later. The method of Willard and McAlpine was then adopted in its entirety and found very satisfactory: Antimony tribromide is prepared in an atmosphere of nitrogen and distilled in a vacuum into a bulb which is sealed, weighed, and finally broken under a solution of tartaric acid; the quantity of bromine is then estimated by conversion into silver bromide, the amount of silver required being determined nephelometrically or weighed as bromide. Reference is only made to details in procedure when this differs in any way from that given by the above authors. The whole of the apparatus used in the course of the experiments was constructed from Pyrex or the very resistant T-glass of Greiner and Friedrichs.

Preparation of Materials.—The water, bromine, potassium bromide, sodium chloride, nitric acid, tartaric acid, and sodium and potassium cyanides required in this research were purified by the methods given by Willard and McAlpine. Silver was prepared from silver nitrate according to the procedure of Richards and Wells (*J. Amer. Chem. Soc.*, 1905, **27**, 459), but in most of the experiments Johnson and Matthey's " chemically pure " silver was used after being washed with absolute alcohol and ether and fused on a lime support, for the two samples were found to give almost identical results.

Hydrogen was generated by electrolysis of a 15% solution of sulphuric acid between platinum electrodes, and purified by passage over heated platinised asbestos and copper gauze, bubbling through a 20% solution of caustic potash containing some dissolved lead oxide, and drying by passage over phosphorus pentoxide (see Noyes, *Bull. Bureau Standards*, IV, 179).

Nitrogen was prepared in an all-glass apparatus by passing a mixture of air and ammonia over heated copper, and purified according to the method of Richards and Krepalka (*J. Amer. Chem. Soc.*, 1920, **42**, 2225).

Balance and Weighing.—A long-beam Oertling balance was employed. Successive weighings of the same object, which were made by substitution, agreed to 0·02 mg. The weights were carefully calibrated, and counterpoises were used whenever necessary. Calcium chloride was kept in the balance case and 50% humidity was assumed when calculating the vacuum correction.

Preparation of Antimony.—Five specimens of antimony were prepared from the following sources: (1) Kahlbaum's purest antimony trioxide, (2) stibnite from the Mysore State, (3) cervantite from the same area, (4) stibnite from the Amherst District in Burma, and (5) stibnite from the Southern Shan States.

The method of preparation of the metal was the same in all the cases. About 500 g. of the finely powdered material were digested

with hot concentrated hydrochloric acid in successive portions until extraction was practically complete. The excess of acid was distilled off and the antimony trichloride distilled 4 or 5 times. It boiled regularly at 210—211°/680 mm., and was always obtained as a clear, pale yellow liquid solidifying to an ivory-white solid. The further steps were according to the method devised by Groschuff (*Z. anorg. Chem.*, 1918, **103**, 168): The trichloride is treated with chlorine and hydrogen chloride to give chloroantimonic acid, $SbCl_5,HCl,\frac{1}{2}H_2O$; this is dissolved in a little water, and large dilution with water then precipitates antimonic acid, which is washed, evaporated to dryness with nitric acid to expel the last traces of chlorine, and ignited. The oxide thus obtained is reduced with sodium cyanide in a porcelain beaker in a muffle furnace at about 650°. The buttons of metal obtained are cleaned as recommended by Muzaffar, powdered in an agate mortar, dried in a current of hydrogen at 400°, and sealed in the containing tube.

Preparation of Antimony Bromide.—Antimony bromide was prepared exactly according to Willard and McAlpine's instructions, the only modification being the use of a mercury-vapour pump for the complete evacuation of the apparatus.

Purity of the Silver.—As a check on the purity of the silver, the ratio AgCl : Ag was determined by following exactly the procedure of Richards and Wells (*loc. cit.*). This work, and all subsequent operations in which silver salts were involved, was done in a special laboratory illuminated by ruby light. Table I shows the results of several determinations.

TABLE I.

Ratio AgCl : Ag.

Wt. of Ag, g.	Wt. of AgCl, g.	100 × AgCl/Ag.	Wt. of Ag, g.	Wt. of AgCl, g.	100 × AgCl/Ag.
7·49956	9·96437	132·866	7·57600	10·06474	132·850
7·41387	9·85066	132·867	7·74410	10·32871	132·862
7·59879	10·09663	132·870	7·48068	9·93930	132·866

The first two experiments were made with silver from silver nitrate, and the remainder with Johnson and Matthey's pure silver, which is evidently of a remarkable degree of purity for a commercial article. The mean value obtained by Richards and Wells was 132·864, and thus the agreement is as close as can be expected.

Weighing and Analysis of Antimony Bromide.—In this part of the work, also, the general method adopted was the one used both by Willard and McAlpine and by Hönigschmid. After being cleaned and dried as recommended by Baxter (*Proc. Amer. Acad. Arts Sci.*, 1924—25, **60**, 228), the bulb containing the antimony bromide was suspended from the balance by means of a platinum wire and

weighed in air and under water. The platinum wire also was weighed in air and in water with the same portion of it immersed as when the bulb was weighed under water. The bulb was then broken with a Pyrex rod under a solution of tartaric acid (250 c.c. of 4—5% solution) in a thick-bottomed, tall beaker. Solution was complete in about 10 hours.

In Expts. Nos. 1—6, the solution was passed through a Gooch crucible to collect the glass. Subsequently, a silica crucible with a porous sintered bottom was used and proved much more satisfactory. In both cases, the glass was ignited to a dull red heat before weighing. Its density was determined and found to be 2·56 g. per c.c. (T-glass).

The analysis of the antimony bromide was effected by determination of the ratio $SbBr_3 : 3AgBr$, and in two cases of the ratio $SbBr_3 : 3Ag$ in addition. For the latter purpose a nephelometer of the Kober type with a Klett top-reader was used.

The gravimetric determination was at first (Expts. 1—6) carried out exactly in accordance with the description given by the authors already mentioned. A Gooch crucible was used, and the solution was refiltered through a small filter-paper to secure any particles of asbestos. As the volume of the solution was about 700 c.c., this was a tedious operation. A great improvement was effected by the use of a Jena-glass crucible with a sintered bottom. In these experiments, the silver bromide was dried for 14—18 hours at 180°, and the moisture content determined by fusing the bulk of the precipitate in a porcelain crucible. Subsequently, the drying was conducted at 300° for 12—18 hours, as recommended by Hönigschmid, and the loss on fusion of the bromide was then found to be negligible, so that it was not determined in every case. The bromide was, however, always fused and its appearance after fusion noted; it was found that when dark spots or a discoloration appeared (due to traces of silver nitrate) a low value for the atomic weight was usually obtained. Such experiments are distinguished by an asterisk in the following table, and are not included in calculating the means. In all other cases, the fused silver bromide was quite clear.

Table II gives the results of the determinations. For calculating the atomic weight, the values Ag = 107·880, Br = 79·920 have been adopted.

In Expts. 7 and 8, the ratio $SbBr_3 : 3Ag$ was determined by the nephelometer before filtering the silver bromide. The values 121·751 and 121·735 were found for the atomic weight, the agreement with the gravimetric value being fair. It was not, however, considered necessary to determine this ratio in every case, as it is sufficient for

TABLE II.

Expt. No.	Wt. of $SbBr_3$, g.	Wt. of AgBr, g.	$SbBr_3$: 3AgBr.	Atomic weight of Sb.
		Kahlbaum's Antimony Trioxide.		
1	4·44079	6·92064	0·641664	121·753
2	3·15437	4·91639	0·641603	121·719 *
3	3·64246	5·67747	0·641566	121·701 *
4	3·97152	6·18954	0·641650	121·746
5	3·47255	5·41185	0·641654	121·750
6	3·80868	5·93549	0·641679	121·762
7	3·44766	5·37296	0·641669	121·756
8	4·12164	6·42335	0·641665	121·754
				Mean 121·754
		Mysore Stibnite.		
9	4·29146	6·68901	0·641569	121·700 *
10	4·03746	6·29236	0·641645	121·743 *
11	3·85444	6·00720	0·641637	121·738
12	4·25750	6·63517	0·641656	121·749
13	4·16876	6·49684	0·641659	121·751
14	3·40170	5·30160	0·641636	121·738
				Mean 121·744
		Mysore Cervantite.		
15	3·35625	5·23081	0·641631	121·735
16	3·98107	6·20437	0·641659	121·751
17	3·82381	5·95934	0·641650	121·746
				Mean 121·744
		Amherst Stibnite.		
18	4·61169	7·18715	0·641657	121·750
19	4·61851	7·19785	0·641651	121·746
20	4·11282	6·40990	0·641635	121·737
21	3·50233	5·45818	0·641666	121·755
22	3·98801	6·21524	0·641650	121·745
				Mean 121·747
		S. Shan States Stibnite.		
23	3·74847	5·84185	0·641658	121·750
24	4·94145	7·70114	0·641652	121·747
25	3·82442	5·96012	0·641668	121·756
				Mean 121·751

the present purpose to compare the relative values for the different samples of antimony, the absolute value of the atomic weight being of secondary importance.

The mean results show an extreme variation of 0·010 in the atomic weights; this is considerably less than the variation among individual experiments and may reasonably be ascribed to experimental error. The difference between these results and those of Muzaffar is considerable, this author having found a variation of 0·93 unit in the atomic weight of different samples of antimony. His individual results are not very concordant, the ratio 3Sb : $KBrO_3$ ranging from 2·1802 to 2·1875 in the case of one sample, corresponding with 0·41 unit in the atomic weight, whilst the preliminary determination of the ratio $3As_4O_6$: $4KBrO_3$ gave results fluctuating

over a range of 0·4%, showing that one of these materials was not very pure, or that the end-point of the reaction was not definite.

An attempt was made to investigate the bromate method as conducted by Muzaffar, but a difficulty was experienced in dissolving the pure antimony in concentrated sulphuric acid except by very prolonged boiling. On cooling, the mass became semi-solid, and although solution could be effected by the addition of a little water, too much water produced a precipitate and transference was troublesome. As Muzaffar gives no details of manipulation, it was considered preferable to make use of a method which had been fully described and experiments by the bromate method were not continued.

Summary.

The atomic weight of antimony has been determined in five samples, one from Kahlbaum and the others from India and Burma. Willard and McAlpine's method was used, and the results ranged from 121·744 to 121·754. These are in good agreement with the best previous determinations; there is no indication that the variation is due to a change in atomic weight, and in any case such variation does not exceed 0·01 unit for the samples examined.

In conclusion, I wish to express my gratitude to Professor H. E. Watson for his valuable suggestions during the course of this work, and to the Directors of Geology of the Governments of India and of Mysore for their kindness in supplying the necessary ores of antimony.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE, INDIA. [*Received, August 9th*, 1927.]

CCCXXXIX.—*Studies of Dynamic Isomerism. Part XXIV. Neutral-salt Action in Mutarotation.*

By THOMAS MARTIN LOWRY and GILBERT FREEMAN SMITH.

Neutral Salt Action in Catalysis by Acids.

THE idea of " neutral salt action " in catalysis by acids arose in the first instance from the observation of Arrhenius (*Z. physikal. Chem.*, 1889, **4**, 226) that the rate of inversion of sucrose by weak acids was augmented by the addition of neutral salts of strong acids, such as potassium chloride, which, at a concentration of $N/8$, increases the catalytic activity of $N/40$-acetic acid by 12·6%. Since neutral salts are not themselves catalysts for the inversion of sucrose, this effect was attributed by Arrhenius to the indirect action of the salt in *increasing* the ionising power of the medium and therefore the ionisation of the weak acid; a similar increase of

the catalytic activity of hydroxyl ions by neutral salts has been postulated by Senter (J., 1907, **91**, 460), and by Osaka (*Z. physikal. Chem.*, 1900, **35**, 661). On the other hand, it has been suggested that neutral salts with a common ion may act by *decreasing* the ionisation of the acid, the undissociated molecules of which are assumed to be catalytically active, as well as the hydrogen ions derived from them. Thus, whereas Arrhenius supposed that only the hydrogen ions act as catalysts, Snethlage (*Z. Elektrochem.*, 1912, **18**, 539; compare Goldschmidt, *Z. physikal. Chem.*, 1912, **81**, 30, and McBain, J., 1914, **105**, 1517) attributed a part of the catalytic activity of the acid to the undissociated molecules, the activity of the molecules and ions being in the ratio $k_m : k_h = 0{\cdot}06 : 1$ for picric acid, but about 2 : 1 for hydrochloric acid. On the other hand, Lapworth (J., 1908, **93**, 2163, 2187) and Dawson (J., 1911, **99**, 1; 1914, **105**, 1093), from a study of the influence of water in diminishing the catalytic activity of acids in alcoholic solutions, concluded that catalysis by acids, so far as it depends on the action of ions, is due to the presence of a mere trace of *free* hydrogen ions, the effect of the *hydrated* hydrogen ions (which are mainly responsible for the conductivity of the acid) being relatively unimportant. This conclusion is directly opposite to that of Kendall (*Proc. Nat. Acad. Sci.*, 1921, **7**, 56), who supposes that the hydrolysis of methyl acetate may be catalysed by compounds of anhydrous hydrogen ions with all the other components of the solution; but it was not intended to exclude catalysis by undissociated molecules of the acid, which was widely advocated by Dawson (J., 1915, **107**, 1426) as the "Dual Theory of Acid Catalysis." More recently, Dawson, who gave for the ratio k_m/k_h values ranging from 1·77 for hydrochloric acid to 0·0034 for acetic acid, has included the anion (but not the metallic kation) of the neutral salt as an independent catalyst, the acceleration produced by these anions being formulated as an inherent property of the ion, comparable with the independent catalytic activity of the hydrogen and hydroxyl ions.

The most important feature of Dawson's work is his repudiation of Arrhenius's hypothesis that the catalytic activity of the ions of a neutral salt is a secondary effect, which is produced only indirectly by stimulating the catalytic activity of some other ion. Each active component is therefore represented by an independent term in his equations. Moreover, Dawson found that he could make use of the *concentrations* of the various components, without attempting to convert them into *activities*. Finally, Dawson's results have attracted widespread attention by reason of their precise quantitative character, which can be illustrated by quoting the catalytic coefficients ($\times 10^6$) deduced from a study of the

velocity of iodination of acetone in presence of sodium acetate and acetic acid, *viz.*,

$$OH' = 10^7;\ H' = 442;\ Ac' = 4{\cdot}5;\ HAc = 1{\cdot}5.$$

The authors of the present paper desire to put on record the fact that, whilst the theory set out in Part XXV (following paper) is a logical development of views advanced in previous papers of this series, the experiments now described were suggested directly by analogy with Dawson's observations on acetone. The analogies that have been detected afford confirmation of the view (which is still based on theory rather than on direct experiment) that the iodination of the ketone and the changes of rotatory power of the sugar are both dependent on a prototropic change, in marked contrast, for instance, to the isomeric change of *N*-chloroacetanilide, which has been shown to depend on a process of reversible chlorination (*Rep. Brit. Assoc.*, 1910, 85).

Neutral-salt Action in Mutarotation.

The influence of neutral salts on the mutarotation of the reducing sugars has received but little attention, perhaps because the changes of rotatory power proceed so rapidly, even in pure water, that a relatively small acceleration makes the velocities too great for accurate measurement. Ample evidence is available, however, to show that, whilst bases and acids (and even water) are powerful catalysts, no marked acceleration is produced by neutral salts of the type of sodium and potassium chlorides (Lowry, J., 1903, **83**, 1317; Worley, *J. Physical Chem.*, 1927, **31**, 882). Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 389) have indeed plotted a curve showing the influence of sodium chloride on the velocity of mutarotation of glucose at 25° over a range of acidity and alkalinity from p_H 1 to 7·7. The influence of this salt is shown to be almost negligible throughout, although definite catalytic effects were attributed to the anions of the weak acids which were present in certain buffer solutions.

The experiments that have just been cited leave the impression that neutral salts in general exert only a negligible effect on mutarotation, and that the velocity of mutarotation is determined mainly, even if not quite exclusively, by the acidity or alkalinity of the solution, as represented by its "hydrogen-ion concentration." This view is expressed in a precise mathematical form in Hudson's well-known equation (*J. Amer. Chem. Soc.*, 1907, **29**, 1571), in which the velocity of mutarotation of glucose at 25° is given by

$$k^* = 0{\cdot}0096 + 0{\cdot}258[\overset{+}{H}] + 9750[\bar{O}H].$$

* Calculated by the use of logarithms to the base 10.

This equation represents the observed velocities of mutarotation as depending on the sum of two variable terms, representing respectively the catalytic activity of *hydrogen ions* and of *hydroxyl ions*, together with a constant term which can be attributed to the action of *neutral water*. It has been adopted (with slightly different constants) by Kuhn and Jacob (*loc. cit.*), who write

$$k = 0{\cdot}0104 + 0{\cdot}334[\overset{+}{\mathrm{H}}] + 9345[\bar{\mathrm{O}}\mathrm{H}],$$

and has been generally accepted as an adequate expression of all the relevant facts. This is made even more striking if the velocity of mutarotation is plotted against the p_{H} values of the solution, in the form of a " catalytic catenary " (Nelson and Beegle, *J. Amer. Chem. Soc.*, 1919, **41**, 559; Kuhn and Jacob, *loc. cit.*; Euler, *Z. anorg. Chem.*, 1925, **146**, 45; 1926, **152**, 113). The resulting curve falls to a shallow minimum at p_{H} 5, and rises steeply on each side in order to show the rapid increase of velocity which is observed in acid or alkaline solutions for which $p_{\mathrm{H}}<2$ or >8, *i.e.*, at concentrations of acid or alkali greater than $N/100$ or $N/1{,}000{,}000$, respectively. The purpose of the present paper is to prove by direct experiment that the algebraic and the geometric methods of representation are alike inadequate, unless the catalytic activity of at least three other possible components of the solution is also taken into account.

Experimental.

(a) *Materials.*—The glucose included a sample recently used in establishing a standard value for the velocity coefficient of the pure sugar (Richards, Faulkner, and Lowry, this vol., p. 113), together with a similar sample which had been purified and tested in the same way. The sodium acetate was thrice recrystallised from distilled water. Acetic acid was distilled from 2% chromic anhydride (Orton and Bradfield, J., 1924, **125**, 960), and on redistillation the fraction of b. p. 116—118° was collected; after freezing, it melted at 16·2°, and therefore contained about 0·2% of water. Hydrochloric acid (approximately $0{\cdot}2N$) was standardised by estimating the chlorine gravimetrically, and was diluted to the required strength with conductivity water. The pyridine had been purified by Dr. I. J. Faulkner for experiments on mutarotation (J., 1925, **127**, 2883). The phenol was colourless and melted at 40°. Sodium carbonate and bicarbonate of " A. R." quality were used without further purification.

(b) *Polarimetric and Electrometric Measurements.*—The velocities of mutarotation were determined in solutions containing 2 g. of glucose in 20 c.c. of the solution at 20°; the velocity coefficients

(k_c) are for time in minutes and for natural logarithms. After mutarotation was complete the p_H values of the solutions were determined by standard methods. When a hydrogen electrode was used, the gas was passed through alkaline permanganate and saturated mercuric chloride solutions, then over electrically-heated palladinised copper, through water, and finally through a solution identical with that under investigation before entering the electrode vessel; the values of the *E.M.F.* recorded for two electrodes in no case differed by more than 1 millivolt. These p_H values were checked by measurements with the quinhydrone electrode, or, when the concentration of electrolytes exceeded 0·1*M*, with the hydroquinhydrone electrode (Biilmann, *Trans. Faraday Soc.*, 1924, **19**, 676). The bicarbonate and carbonate solutions (p_H 7—9) were examined by Dr. W. S. Hughes with a glass electrode, which had been standardised against a phosphate buffer (p_H 6·80) and a borate buffer (p_H 9·24, as determined by means of a hydrogen electrode).

Determination of the Catalytic Catenary for Glucose at 20°.

Since the data of Kuhn and Jacob related to 25°, a fresh catalytic catenary was plotted for 20°, for comparison with the data of Euler (*Z. anorg. Chem.*, 1926, **152**, 113). This was done (as in the experiments of the earlier workers) by using dilute hydrochloric acid and sodium bicarbonate or carbonate to produce the desired degrees of acidity or alkalinity. The electrometric and polarimetric data are set out in Table I, and the velocity coefficients from Table I have been plotted in Fig. 1 against the p_H values of the solutions.

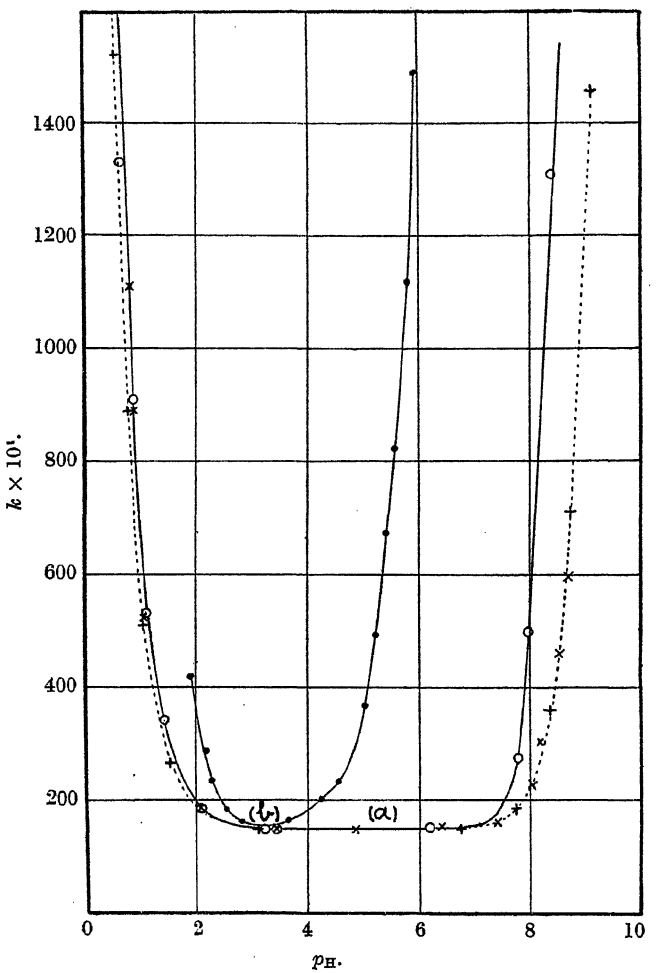
TABLE I.

Mutarotation of glucose in acid and alkaline solutions.

	Hydrogen-ion concentration, p_H.					
Solvent.	Hydrogen electrode.	Quinhydrone electrode.	Glass electrode.	k_c.	k_c — 0·0147.	$(k$ — 0·0147)/c.
0·5*N*-HCl	0·404	—	—	0·216	0·201	0·402
0·4062*N*-HCl	0·483	—	—	0·174	0·159	0·391
0·3*N*-HCl	0·619	—	—	0·133	0·118	0·393
0·198*N*-HCl	0·900	0·88	—	0·0909	0·0762	0·385
0·1*N*-HCl	1·09	1·09	—	0·0529	0·0382	0·382
ca. 0·05*N*-HCl	1·44	1·44	—	0·0338		
0·05*N*-HCl	1·40	—	—	0·0337	0·0190	0·380
0·01*N*-HCl	2·08	2·10	—	0·0184	0·0037	[0·37]
ca. 0·001*N*-HCl	3·23	—	—	0·0147		
ca. 0·0005*N*-HCl	3·42	3·38	—	0·0147		
ca. 0·0001*N*-HCl	6·18	—	—	0·0150		
0·01*M*-$NaHCO_3$	—	—	7·76	0·0274		
0·05*M*-$NaHCO_3$	—	—	7·92	0·0497		
0·001*M*-Na_2CO_3	—	—	8·35	0·131		
0·002*M*-Na_2CO_3	—	—	8·86	0·196		

The velocities measured by Euler at 20°, and by Kuhn and Jacob at 25°, have also been included in the figure, the latter being divided

FIG. 1.

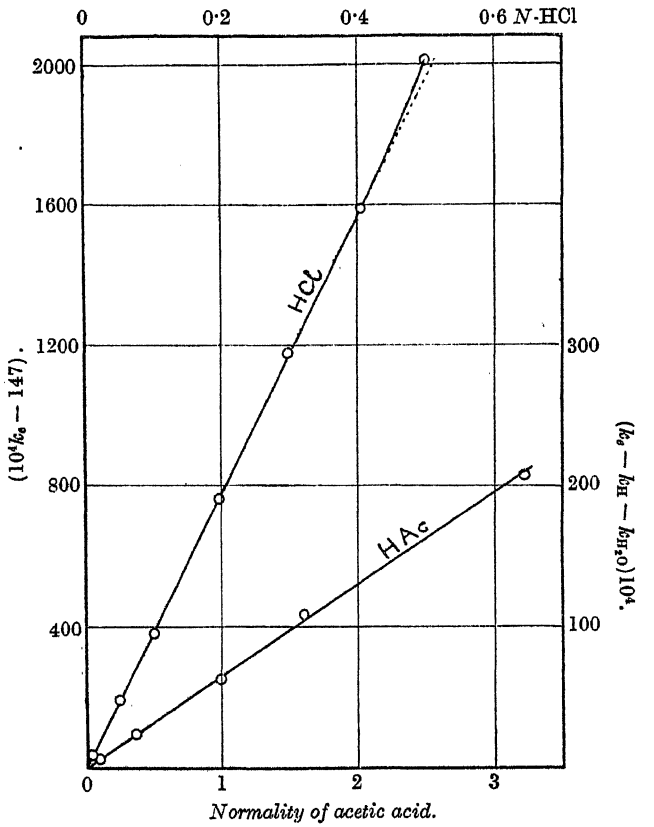


Velocity of mutarotation of glucose at 20° in acid and alkaline solutions: (a) *the hollow circles are for solutions made acid with hydrochloric acid or alkaline with sodium carbonate or bicarbonate. The crosses* (+) *on a dotted curve represent Euler's data for* 20°. *The diagonal crosses* (×) *represent Kuhn and Jacob's data for* 25° *reduced to* 20° *by dividing the velocity coefficients by* 1·65 ; (b) *the black circles are for solutions containing* (i) *various proportions of acetic acid* (*L.H.*), (ii) N/10-*acetic acid with various proportions of sodium acetate* (*R.H.*).

by 1·65 to allow for the difference of 5° in temperature (Hudson and Dale, *J. Amer. Chem. Soc.*, 1917, **39**, 320).

(a) *Acid solutions.* The velocity coefficients and hydrogen-ion concentrations were measured in 10% solutions of glucose in aqueous hydrochloric acid over a range from 0·0001 to 0·5*N*-acid. The p_H values, which were determined with a hydrogen electrode and checked in some cases with a hydroquinhydrone electrode, agree closely in this part of the catenary with those given by the

FIG. 2.



Velocity of mutarotation of glucose at 20° in presence of hydrochloric and acetic acids.

earlier workers; but these electrometric data do not give a very satisfactory constant for the catalytic coefficient of the ion. On the other hand, Fig. 2, in which the increment produced by the acid in the velocity coefficient of the sugar is plotted against the volumetric concentration of the acid, shows a linear relation between these two quantities which persists up to about 0·4*N*, but is then followed by a definite upward curvature. The values of the ratio

$(k_e - 0{\cdot}0147)/c$, which are given in the last column of Table I, show a small progressive increase with increasing concentration, from 0·38 at 0·05N to 0·40 at 0·5N. This increase can be explained quite readily by accepting Snethlage's view that the catalytic coefficient of the undissociated molecules of hydrochloric acid is greater than that of the hydrogen ions derived from them. Since the degree of dissociation of hydrochloric acid in water is about 83% at $N/2$ and 93% at $N/20$, a rough extrapolation to zero concentration would give a limiting value of 0·36 for the catalytic coefficient of the hydrogen ion at 20°. This agrees closely with the coefficient given by Hudson, which is about 0·36, when reduced to base e and divided by 1·65 to correct for the difference of 5° in temperature. A much rougher estimate shows that, since the catalytic coefficient of the acid is increased in the ratio of 19 : 20 when the ionisation is decreased from 93 to 83%, that of the undissociated molecules of the acid must be about half as great again (1·53 : 1) as that of the hydrogen ions derived from them, in close agreement with the ratio 1·55 : 1 deduced by Dawson in 1915.

(b) *Alkaline solutions.* On the alkaline side, the quinhydrone electrode is no longer trustworthy, and the hydrogen electrode is subject to error as a result of the displacement of carbon dioxide from the solutions by hydrogen. We have therefore based our calculations on a series of determinations by Dr. W. S. Hughes, in which a glass electrode was used. The alkaline arm of our catenary is therefore notably different from that of the catenaries plotted by Kuhn and Jacob, and by Euler, which are practically coincident when allowance is made for the different temperatures at which their measurements were made. We believe, however, that the velocities now recorded for the mutarotation of glucose in alkaline solutions ($p_H > 7$) are free from a source of error that was previously present, and are therefore more trustworthy than those published hitherto. Whilst, however, it is possible to deduce a satisfactory value for the catalytic activity of the *hydrogen ion* from measurements of the velocity of change in a dilute solution of a strong acid, this cannot be done in the same simple way in the case of the *hydroxyl ion* of an alkali because (i) the concentrations of alkali that are required to produce a given velocity are about 30,000 times smaller than in the case of an acid, and (ii) a very dilute solution of a free alkali inevitably becomes carbonated, and to an unknown extent, by the carbon dioxide of the atmosphere. The required degree of alkalinity can therefore only be maintained by using a "buffer solution"; and, as Kuhn and Jacob have shown, the anion of the buffer solution may have a catalytic activity which is comparable in magnitude with that of the trace of hydroxyl

ions which the solution contains. Since precisely the same considerations must apply to a carbonate or bicarbonate as to a phosphate or citrate, it is clear that solutions that have been made alkaline with sodium carbonate or bicarbonate cannot be used to give an exact value for the catalytic activity of the hydroxyl ion, unless a correction is made for the catalytic activity of the carbonate and bicarbonate ions, of which the concentrations are uncertain and the specific catalytic activities unknown. We therefore merely put on record the fact that the catalytic coefficient of the hydroxyl ion is probably less than $k_e = 20{,}000$, since this number includes the catalytic activity of the bicarbonate ions as well as of the hydroxyl ions; but we are not yet prepared to put forward a more definite value.

(c) *Neutral solutions.* The concentrations of the hydrogen and hydroxyl ions at the isoelectric point are so small that their effect on the velocity of mutarotation of the sugar (as calculated from the effects produced by higher concentrations of acid or alkali) is only of the order of 1×10^{-5}, and is therefore quite inappreciable. This is true, not only at the isoelectric point, but over a considerable range on either side, so that the central part of the catalytic catenary is almost horizontal over the range p_H 3—7. The actual velocity of mutarotation at the isoelectric point, however, so far from being inappreciable, is only a little less than it is in neutral water, where the influence of the ions should be about 100 times greater than at the isoelectric point. Thus Hudson's equation gives a velocity coefficient $k = 0{\cdot}0106$ for glucose in neutral water at 25°, falling to a minimum value of $k = 0{\cdot}0097$ at the isoelectric point; the velocity at the isoelectric point is therefore 91·5% of that in neutral water. In the same way, the minimum velocity, $k = 0{\cdot}01041$, calculated from the equation of Kuhn and Jacob is 92% of the velocity, $k = 0{\cdot}01133$, in neutral water. These authors therefore concur in postulating a diminution of about 8% in the velocity of mutarotation of glucose in feebly acid solutions. On the other hand, this effect was not observed by Andrews and Worley (*J. Physical Chem.*, 1927, **31**, 882). In the present series of experiments, our own measurements have given a velocity coefficient $k_e = 0{\cdot}0147$ at p_H 3·23 and 3·42, and $k_e = 0{\cdot}0150$ at p_H 6·18, as contrasted with the standard value $k_e = 0{\cdot}0146$ in neutral water at 20°. These measurements therefore afford no experimental confirmation for the very plausible theoretical view that the velocity coefficient in feebly acid solutions should be rather less than in pure water; and it is noteworthy that Euler also does not record any value less than 0·0146 for the velocity coefficient of glucose at 20°, although his measurements at 5·2° show a well-marked minimum.

Determination of the Catalytic Coefficient of an Undissociated Acid.

The catalytic coefficient of the undissociated molecules of a strong acid is difficult to detect, because this component only becomes important at high concentrations, when the velocity of mutarotation is too great for accurate measurement. We can, therefore, only put on record a general statement to the effect that the catalytic coefficient of the undissociated molecules of hydrochloric acid is apparently about 1·5 times as great as that of its ions. In the case of a weak acid, such as acetic acid, however, a fairly accurate value for the catalytic coefficient of the undissociated acid can be deduced from the measured velocities of mutarotation of glucose in solutions of the acid. The data for 10% solutions of glucose in acetic acid over the range 0·1—3·22N are set out in Table II and plotted in Fig. 2.

TABLE II.

Mutarotation of glucose in dilute acetic acid at 20°.

Conc. of acetic acid, N.	p_H.	k_e.	k_h.	$k_e - k_h$.	$(k_e - k_h)/c$.
3·22	1·87	0·0416	0·0208	0·0208	0·0065
1·61	2·17	0·0284	0·0175	0·0109	0·0068
1·00	2·26	0 0233	0·0170	0·0063	0·0063
0·370	2·54	0·0182	0·0158	0·0024	0·0065
0·100	2·78	0·0158	0·0152	0·0006	—

In Fig. 2 the velocity coefficients have been diminished by an amount equal to the value of the coefficient in dilute hydrochloric acid of equal electrometric activity, and the differences have been plotted against the normality of the acetic acid. The relation between these two quantities is linear over the whole range of concentrations. This difference is a measure of the catalytic activity of the acid, after allowing for the catalytic activity of the hydrogen ions and of the water in the solution. Since the acid is ionised only to a very small extent (about 1%) even in the most dilute solutions, the constant ratio shown in the last column of Table II gives the catalytic coefficient of the undissociated acid, $k_e = 0{\cdot}0065[\mathrm{HAc}]$.

Determination of the Catalytic Coefficients of Anions and Kations.

Although the equations of Hudson and of Kuhn and Jacob contain a "neutral water" term (which is not present in Dawson's equation), there is nothing in their equations to correspond with Dawson's "anion" term. This omission is all the more remarkable in view of the observations made by Kuhn and Jacob on the catalytic activity of buffer solutions. A most important feature

of the present experiments, therefore, was an attempt to discover the existence of an "anion" term in mutarotation, and to determine its magnitude in some particular case. It was already clear from earlier observations that the ions of sodium and potassium chlorides had no marked catalytic properties; but we anticipated on theoretical grounds that the anion of a weak acid might possess appreciable catalytic activity. A difficulty immediately arises, however, from the fact that the salts of a weak acid are hydrolysed to an extent which increases as the dissociation constant of the acid diminishes; moreover, the catalytic activity of the hydroxyl ions resulting from this hydrolysis is so enormous that it would entirely mask any small catalytic activity due to the anion of the acid, unless the latter were present at relatively enormous concentrations. For this reason we adopted the device of adding to the neutral salt (*N*-sodium acetate solution) a quantity of the free acid (*N*/10-acetic acid) sufficient to make the reaction of the solution definitely *acid* instead of *alkaline*. The ideal condition would, of course, be to work at the isoelectric point, where the velocity of mutarotation (in the absence of some catalytically active ion other than hydrogen and hydroxyl) would be, if anything, rather less than in pure water.

(a) *Catalytic coefficient of the acetate ion.* Our first experiment showed that a solution of glucose in *N*-sodium acetate gave a velocity coefficient, $k_e = 0{\cdot}0982$ at 20°, which was nearly *seven* times as great as in neutral water ($k_e = 0{\cdot}0146$ at 20°). In this case an acceleration was inevitable in view of the alkaline character of the salt; but this explanation was no longer possible in a second experiment in which the velocity coefficient for 0·961*N*-sodium acetate, *in a solution acidified with* N/10-*acetic acid* to p_H 5·54, was found to be $k_e = 0{\cdot}0822$, or about *six* times as great as in water. In this experiment, if hydrogen and hydroxyl ions and neutral water had been the only catalysts in the solution, the velocity coefficient would have been $k_e = 0{\cdot}0147$; and a correction for the catalytic activity of the undissociated molecules of acetic acid would have increased this only to $k_e = 0{\cdot}0153$. This number is rather less than one-fifth of the velocity coefficient actually observed, and, since the sodium ion is known to be inactive, the other four-fifths of the observed velocity must have been due to the *acetate ion*, which was thus shown to be an active catalyst for the mutarotation of the sugar.

Table III gives the velocity coefficients and p_H values for a series of solutions containing *N*/10-acetic acid, with various proportions of sodium acetate. The velocity coefficients of these solutions are plotted against the p_H values in the form of a catalytic catenary

TABLE III.

Mutarotation of 10% *glucose in* 0·1N*-acetic acid + sodium acetate at* 20°.

NaAc, N.	p_H.	k_e.	$k_e - 0{\cdot}0153$.	$(k_e - 0{\cdot}0153)/c$.
0·0096	3·64	0·0164	0·0011	—
0·0480	4·25	0·0200	0·0047	—
0·100	4·52	0·0230	0·0077	—
0·300	5·00	0·0365	0·0212	0·071
0·480	5·21	0·0491	0·0338	0·070
0·750	5·41	0·0672	0·0519	0·069
0·961	5·54	0·0822	0·0669	0·070
1·50	5·75	0·119	0·104	0·069
2·00	5·89	0·149	0·134	0·067

in Fig. 1, whilst in Fig. 3 the p_H values are plotted against the concentrations of sodium acetate.

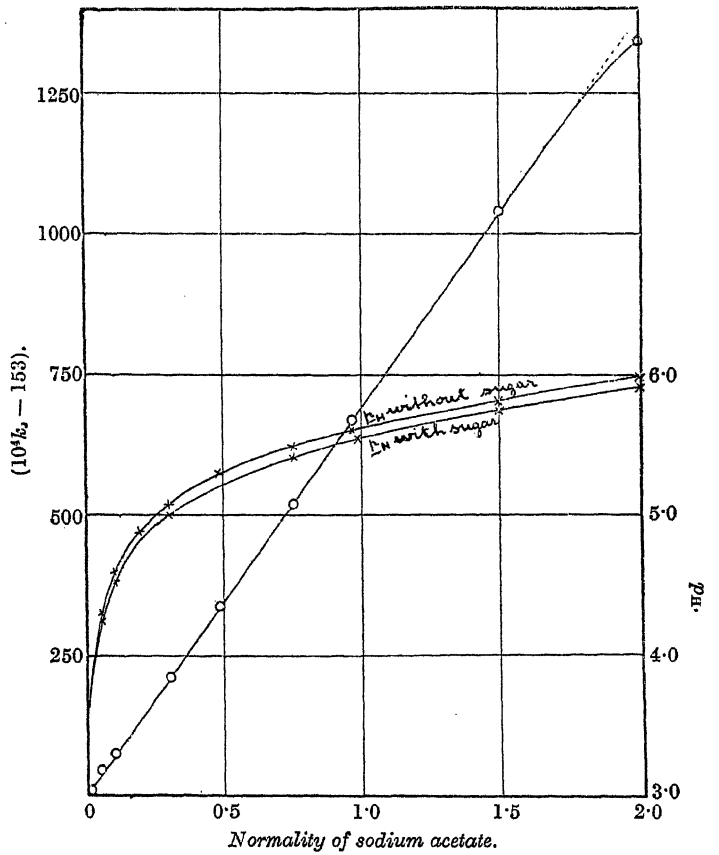
The p_H values plotted in the upper curve of Fig. 3 *for solutions which did not contain any sugar* agree closely with those given by Dawson, but these values were lowered when determined in presence of 10% of glucose by an amount which varied from 0·02 to 0·06 as the concentration of the sodium acetate increased from 0·0096 to 0·3N, and then remained almost constant up to 2N.

The solutions now under consideration were too near to the isoelectric point to exhibit any marked catalysis by hydrogen or hydroxyl ions, but they all contained, in addition to the acetate ion, the catalytically active molecules of water (which would give a partial velocity coefficient of 0·0147) as well as active molecules of N/10-acetic acid (which would give a partial velocity coefficient of 0·0006). Fig. 3 shows that, when the difference between the observed velocity coefficients and a constant partial velocity coefficient of 0·0153 is plotted against the volumetric composition of the sodium acetate, these two quantities are proportional to one another over the range from 0·0096N to 1·5N. The ratio $(k_e - 0{\cdot}0153)/c$, which is given in the last column of Table III, tends to increase in the most dilute solutions; but, over the range from 0·3N to 2·0N, it gives an average value for the catalytic coefficient of the acetate ion, $k_e = 0{\cdot}069$. In Dawson's experiments on the iodination of acetone, the catalytic coefficient of the acetate ion was about 3 times as great as that of the undissociated molecule of acetic acid, but the ratio of the two coefficients, when deduced from a study of their influence on the mutarotation of glucose, is rather greater than 10 to 1.

(b) *Catalytic coefficient of the ammonium ion.* Theoretical reasons led us to suppose that catalytic activity need not be confined to the *anion* of a salt, but that a *kation* might possess similar catalytic powers, provided that it could be classed as a proton donator. We therefore determined the velocity of mutarotation of glucose

in a *N*-solution of ammonium chloride, and found that, although the hydrogen-ion concentration of the solution (p_H 4·7) coincided almost exactly with the isoelectric point, the velocity coefficient, $k_e = 0{\cdot}0159$ at 20°, was actually 8% greater than in neutral water. The catalytic coefficient of the ammonium ion as deduced from

FIG. 3.



Velocity of mutarotation and p_H *values for solutions of glucose in* N/10*-acetic acid with various concentrations of sodium acetate.*

this experiment is approximately 0·0012. This is about one-fifth as great as the coefficient for undissociated acetic acid, but sixty times smaller than that of the acetate ion.

Catalytic Coefficients of Neutral Salts.

A comparison of the "acetate" catenary of Fig. 1 with the "carbonate" catenaries previously deduced from the behaviour of

carbonate and bicarbonate solutions is very instructive, since it shows the relatively small part that is played by the feeble acidity or alkalinity (p_H 2 to 8) of a buffer solution in determining the velocity of mutarotation of the sugar, and the enormous influence of the neutral or saline components of the solution. In order, however, to dissipate finally the idea that the velocity of mutarotation is determined predominantly by the acidity or alkalinity of the solution, or by its hydrogen-ion concentration, a number of measurements were made with aqueous solutions of glucose containing a salt of a weak acid and a weak base, under conditions which ensured that the hydrogen-ion concentrations were either approximately equal to that of neutral water or intermediate between that of neutral water and the isoelectric point. Since the velocity coefficients calculated from the equations of Hudson or of Kuhn and Jacob are substantially constant from p_H 3 to p_H 7, any solution in this range might be expected, on the basis of these equations, to give a velocity coefficient equal to, or slightly less than, that observed in neutral water; on the other hand, if our theoretical views were well-founded, it appeared likely that *a neutral solution containing the neutral salt of a weak acid and base* would change much faster than a neutral solution in pure water, or than a neutral solution containing only a neutral salt of a strong acid and base.

(a) *Ammonium acetate.* This prediction was tested by measuring the velocity of mutarotation of glucose in presence of *N*-sodium acetate and *N*-ammonium chloride. Since sodium chloride produces no important changes of velocity, this solution was equivalent to one containing *N*-ammonium acetate. As we anticipated, the sugar in this *neutral* solution changed even more rapidly than in a solution containing only *N*-sodium acetate, which has a strongly *alkaline* reaction, or in a solution of ammonium chloride, which is definitely *acid* in its reaction. The velocity coefficient, $k_e = 0{\cdot}106$ at p_H 6·66, was found to be *more than seven times* as great as in neutral water. It is also about 25% greater than the value, $0{\cdot}0147 + 0{\cdot}0012 + 0{\cdot}069 = 0{\cdot}085$, calculated by adding together the catalytic coefficients of neutral water and of the ammonium and acetate ions. This acceleration, which can be attributed to the " hydrolysis " of the salt to free ammonia and free acetic acid, was in accord with the expectations which we had formed in view of the increase in the amphoteric properties of the solution, which would result from the simultaneous presence of the weak acid and the weak base. The approximate value of the catalytic coefficient of the salt in its various forms is 0·091.

(b) *Pyridine and phenol.* The neutral-salt effect described in the preceding paragraph (which is of a totally different character

from that postulated by Arrhenius, since the increment of velocity produced by the neutral salt was 626% instead of only 12·6%) would obviously become negligible if the acid and base were so weak as no longer to exhibit any appreciable acid or basic properties; it is also known to be negligible when the acid and base are both strong. The effect must therefore rise to a maximum at some intermediate value of the dissociation constants. For this reason, the experiment was repeated, but with phenol and pyridine as the acid and base in place of acetic acid and ammonia. The relevant dissociation constants are set out below, whilst the velocity coefficients and p_H values are included in Table IV.

Acid dissociation constant, K_a.		Basic dissociation constant, K_b.	
Phenol :	$1{\cdot}1 \times 10^{-10}$ at 18° or 25°	Pyridine :	$1{\cdot}6 \times 10^{-9}$ at 18° $2{\cdot}3 \times 10^{-9}$ at 25°
Acetic acid :	$1{\cdot}8 \times 10^{-5}$ at 18° or 25°	Ammonia :	$1{\cdot}75 \times 10^{-5}$ at 18° $1{\cdot}8 \times 10^{-5}$ at 25°

TABLE IV.

Mutarotation of glucose in presence of a weak acid and base.

Solvent.	p_H.	Velocity coefficient at 20°.
N-Sodium acetate	—	0·0982
N-Ammonium chloride	4·7	0·0159
N-Sodium acetate + *N*-Ammonium chloride	6·66	0·106
0·5*N*-Phenol	5·8	0·0146
0·1*N*-Phenol	6·21	0·0147
0·1*N*-Pyridine + 0·1*N*-Phenol	7·48	0·0447

Since phenol is not sufficiently soluble to give a *N*-solution, the acid and base were used at *N*/10-concentrations, and gave a velocity coefficient, $k_e = 0{\cdot}0447$ at 20° for p_H 7·48. The velocity coefficient was therefore 3 times as great as in water, although the p_H was changed by less than 0·5 unit from that of neutral water. If the slight alkalinity of the solution had been produced by a trace of sodium bicarbonate, the velocity coefficient would have been about 0·0175, or about 40% of that actually observed; the other 60% must therefore be due to the *N*/10-pyridinium phenoxide. The catalytic coefficient of the pyridinium salt as deduced from these data is roughly 0·272. It is noteworthy that the catalytic coefficient of the pyridinium salt in *N*/10-solution is about 3 times as great as that of ammonium acetate in *N*-solution, and is very nearly as large as that of the hydrogen ion, although it is still not so great as that of the undissociated molecules of a strong acid.

Summary.

(*a*) Although the mutarotation of glucose is catalysed by acids and bases, as well as by water, it is not affected appreciably by neutral salts of the type of sodium chloride.

(*b*) Definite catalytic activity has been detected, however, in (i) the undissociated molecules of a strong or weak acid, (ii) the anion of a weak acid, and (iii) the kation of a weak nitrogenous base.

(*c*) The catalytic coefficients of these components are

$$[HCl] \text{ about } 0{\cdot}5; \quad [\overset{+}{N}H_4] = 0{\cdot}0012;$$

$$[HAc] = 0{\cdot}0065; \quad [\bar{A}c] = 0{\cdot}069.$$

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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CCCXL.—*Studies of Dynamic Isomerism. Part XXV. The Mechanism of Catalysis by Acids and Bases.*

By THOMAS MARTIN LOWRY.

Catalysis of Mutarotation by Acids and Bases.

THE fact that mutarotation, like so many other chemical changes, is not a spontaneous process, but depends on the presence of a catalyst (Lowry, J., 1899, **75**, 211), compels us to seek an explanation of the part played by the catalyst in effecting the change, and in particular to discover a reason for the unique efficiency of water as a solvent for the mutarotation of the sugars, and for the still more remarkable catalytic activity of acids and bases. The earliest suggestion (*ibid.*, p. 219) postulated that mutarotation could be initiated by any oxygenated solvent, since the changes of rotatory power in these solvents were usually very rapid when compared with the slow changes observed in hydrocarbons and in analogous solvents such as chloroform. This view became untenable, however, when it was found that the mutarotation of nitrocamphor could be "arrested" by adding a trace of carbonyl chloride to *ether*, in order to eliminate basic impurities (Lowry and Magson, J., 1908, **93**, 119). It was then pointed out that catalytic solvents all appeared to be of the type HX, and that solvents from which a hydrogen atom cannot be eliminated easily are not able to initiate isomeric change, although (as in the case of ether) they may contain oxygen, and may even possess ionising properties (*ibid.*, p. 132). Subsequent investigations (Lowry and Richards, J., 1925, **127**, 1385; Lowry and Faulkner, *ibid.*, p. 1883) showed that, although dry pyridine had been repeatedly cited as an effective catalyst for the mutarotation of glucose (Behrend and Roth, *Annalen*, 1904, **331**, 361), pyridine and cresol are alike impotent *in the absence of water*, but that when mixed with one another they develop a catalytic activity which is

far greater than that of water itself. The view was therefore advanced that the prototropic changes which give rise to the mutarotation of the sugars can only take place in an amphoteric solvent, *i.e.*, in a solvent which can both accept a proton from the sugar and give a proton back again to it or to its ion.

An entirely different method of approach to the problem is found in the theory put forward by Euler (Euler and Hedelius, *Biochem. Z.*, 1920, **170**, 150; Euler, Myrbäck, and Rudberg, *Arkiv. Kemi Min. Geol.*, 1923, **8**, No. 281) in order to provide a quantitative basis for determining the influence of acids and alkalis on the mutarotation of glucose. Euler supposes (i) that the velocity of mutarotation of glucose is proportional to the volume concentration of its *ions*, and (ii) that these ions are produced by the formation of *salts* of the sugar, on the one hand with alkalis, and on the other with acids. According to this theory, the velocity of mutarotation of the sugar in a solution of given acidity or alkalinity could be calculated from its acid and basic dissociation constants, K_a and K_b, together with the reaction velocities, r_a and r_b, of the anion and kation of the sugar salts; but in practice the calculation can only be carried out in the converse direction, since only one of the four fundamental constants has been measured by an independent method. This one independent constant is the acid dissociation constant of glucose in water at 18°, which was determined electrometrically by Michaelis and Rona (*Biochem. Z.*, 1913, **49**, 232) from the change of "hydrogen-ion concentration" on adding the sugar to a dilute alkali. Euler and Hedelius (*loc. cit.*) measured the velocity of mutarotation of glucose in buffer solutions containing sodium citrate and hydrochloric acid of $N/10$ and $N/100$ concentration, and deduced (by extrapolation to zero concentration of buffer solution) the value $k^* = 0{\cdot}0066$ for the minimum velocity at 20°, and $p_H = 3{\cdot}6$ for the hydrogen-ion concentration at this point of maximum stability of the sugar; they then used the value, $K_a = 6{\cdot}6 \times 10^{-13}$, given by Michaelis for the *acid dissociation constant* of the sugar at 18°, in order to calculate an approximate value, $K_b = 10^{-19}$, for the *basic dissociation constant*, on the assumption that the point of maximum stability is identical with the isoelectric point and that the hydrogen-ion concentration at the isoelectric point is given by the equation $[H^+] = \sqrt{K_a K_w / K_b}$, where K_w is the dissociation constant of water. In two subsequent papers (*Z. anorg. Chem.*, 1925, **146**, 45; 1926, **152**, 113), Euler used his own measurements of the acid dissociation constant of water at 5·2° in order to deduce values for the concentration of the sugar ions and for their reaction velocities at this temperature, which he

* The velocity coefficient calculated from logarithms to the base 10.

supposed to be equal to one another, since he obtained symmetrical catenary curves on plotting the velocity of mutarotation at 5·2° and at 20° against the p_H of the solution. In this way he deduced for the four essential constants at 5·2° the values $K_a = 1 \times 10^{-13}$; $K_b = 2 \times 10^{-18}$; and $r_a = r_b = 38$, the half-change period being therefore 0·45 sec. *for the ion of either sign.*

Euler's ionic theory of mutarotation was at once adopted by Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 389) as the basis for their numerical calculations. These authors made a new series of measurements of the velocity of mutarotation of glucose at 25° in solutions of different degrees of acidity and alkalinity, and showed that it could be expressed by an equation which differed only slightly from that of Hudson. Since this equation contains a term which does not depend on the acidity or alkalinity of the solution, they concluded that the *neutral molecules* of glucose, as well as the kations and anions derived from them, undergo isomeric change. Moreover, since the two arms of their catenary curve were not symmetrical, they concluded that the reaction velocity of the anions and kations are not equal (as Euler supposed) but that the reaction velocity of the anions is 2·1 times as great as that of the kations. They therefore assigned to the reaction velocities at 25° of the neutral molecules of the sugar and of the kations and anions derived from them the values $r_u = 0{\cdot}0104$, $r_b = 54{\cdot}4$, and $r_a = 113{\cdot}2$. The dissociation constants of the sugar at this temperature were given as $K_a = 10{\cdot}5 \times 10^{-13}$ and $K_b = 7{\cdot}8 \times 10^{-17}$.

In his later papers, Euler also adopted the view that mutarotation is not due exclusively to the anion and kation of the sugar, but he suggested that the constant term in Hudson's equation need not necessarily represent the isomeric change of the undissociated molecules of the sugar, since it could also be attributed to a "zwitterion" (or bipolar molecule, compare J., 1925, **127**, 1371) carrying both a positive and a negative charge, or to "some form of glucose which is present at a concentration proportional to that of the uncharged molecules."

It will be seen that, whilst the simple ionic theory of mutarotation can be used to calculate hypothetical values for the ionisation of the sugar, and for the reaction velocities of its ions, it does not provide any numerical data which can be checked by independent experiments. It is, moreover, definitely incompatible with our more recent observations on mutarotation in non-aqueous solutions, and must be rejected for the following reasons:

(i) If the sugar is capable of being ionised by mere dissolution in water, according to the scheme $HS \rightleftharpoons H^{\cdot} + S'$, it must obviously be ionised even more readily to form an ionised pyridinium salt accord-

ing to the scheme $C_5H_5N + HS \rightleftharpoons C_5H_5NH^{\cdot} + S'$, when dissolved in anhydrous pyridine.* If then the ion S′ has a definite reaction velocity, as Euler supposes, this ion must at once undergo isomeric change and give rise to a very rapid mutarotation, since the half-life period of the ion (according to Euler's calculation) is less than a second. In reality, however, nothing of the sort happens, since the mutarotation of tetramethyl glucose in pyridine can be stopped completely over a period of 2 or 3 hours by very moderate purification and drying (Lowry and Richards, *loc. cit.*, p. 1398).

(ii) Conversely, if the sugar is capable of being ionised, either by removal of hydroxyl or by addition of hydrogen, according to the scheme $HOS \rightleftharpoons HO' + S^{\cdot}$ or $S + H^{\cdot} \rightleftharpoons HS^{\cdot}$, it seems certain that this ionisation must be promoted by dissolving the sugar in an acidic solvent, such as cresol, which would form an ionised salt according to the scheme $C_7H_7{\cdot}OH + HOS \rightleftharpoons C_7H_7{\cdot}O' + S^{\cdot} + H_2O$, or $C_7H_7{\cdot}OH + S \rightleftharpoons C_7H_7O' + HS^{\cdot}$. The ionic theory then indicates once more that this ionisation must be followed by a rapid isomeric change, and consequent mutarotation, in accordance with the ordinary laws of mass action and reaction velocity. Actually, however, the velocity of mutarotation of tetramethyl glucose in cresol is almost inappreciable, since it is at least forty times less than in pure water.

(iii) Finally, if the simple ionic theory were correct, mutarotation must inevitably occur *in any ionising solvent*, whereas experience has shown that it is only in the case of media which possess definite amphoteric properties that we can assert with any degree of confidence that the pure solvent is a complete catalyst for mutarotation. Thus, even in the case of methyl alcohol, which is quite a good ionising solvent, the very low velocity coefficient observed by Faulkner and Lowry (J., 1926, 1938) has been reduced about 8-fold in the recent experiments of Worley and Andrews (*J. Physical Chem.*, 1927, **31**, 742), so that the residual velocity of change is now altogether insignificant.

On all these grounds the simple ionic theory of catalysis is seen to be untenable in the light of experiments on mutarotation in non-aqueous solutions.

An Electrolytic Theory of Catalysis.

A mechanism of catalysed mutarotation, which is in harmony with the observations cited above (and which actually led to the experiments by which most of the relevant facts were discovered)

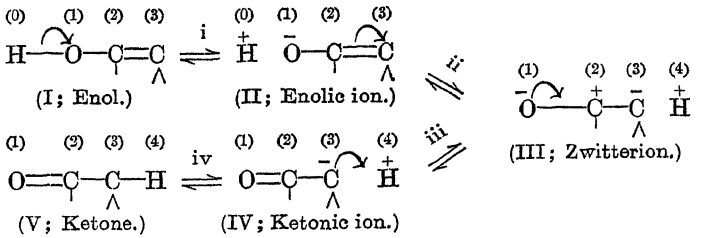
* It is assumed that the pyridine has not been dried so perfectly as to inhibit completely the formation of a salt, as in Baker's experiments on dry ammonia and hydrogen chloride.

was described in 1925 (J., 127, 1371). This mechanism depends on an initial *addition and subtraction of a proton* by a medium possessing both acid and basic properties, giving rise to the formation of a bipolar molecule or "zwitterion"; the rupture of a bond (by the conversion of the covalency into an electrovalency) then produces just those electric charges which are needed to neutralise the charges already present in the bipolar molecule, and thus gives rise immediately to the intermediate aldehydic form of the sugar. Only two additional points are needed in order to make this mechanism cover also Dawson's recent experiments on the iodination of acetone in presence of acids and their salts, as well as the new observations on mutarotation which are described in Part XXIV (preceding paper). These additional points are (i) a clear recognition of the fact that prototropic change involves *a flow of electrons through the molecule*, in addition to the transfer of a proton to and from the medium, and (ii) an extended conception of the meaning of the terms acid and base, to include all those ions and molecules which are able to give or to receive a proton. The isomeric change is then seen to depend on a process which is closely analogous to an electrolysis of the prototropic compound between positive and negative poles provided by the basic and acid components of the medium.

(a) *Electron-migration as a Condition of Isomeric Change.*—It is not generally realised that the process of isomeric change in unsaturated compounds involves a flow of electrons through the molecule, as well as the migration of a radical. It is, however, obvious that, if the *radical* migrates in the form of an *ion*, it must deliver up an electric charge at its new point of attachment, whilst leaving behind a charge of opposite sign at the point of departure; the elimination of these electric charges is therefore an essential feature of the isomeric change. It is then easy to show that the rearrangement of bonds (described by Jacobsen as "desmotropy"), which accompanies isomeric change in unsaturated and conjugated systems, actually consists in a transfer of valency electrons from atom to atom, and that this transfer produces a flow of electrons of precisely the kind that is required to neutralise the charges set up by the migration of the ion.

Since the iodination of acetone, which has formed the basis of Dawson's recent experiments on catalysis, depends on the enolisation of the ketone (Lapworth, J., 1904, 85, 30), it will be convenient to select this type of isomeric change as an illustration of the general proposition set out above. We will therefore suppose that an enol is to be changed into a ketone by an ionic mechanism of the same general character as that postulated by Euler and by Kuhn and Jacob for an action catalysed by bases. The four consecutive

stages (i)—(iv) of such a process may be illustrated by a scheme of the same general character as that already used to represent the mutarotation of a sugar (J., 1925, **127**, 1384), but dissected into a series of steps as follows :



(i) *Ionisation of the enolic compound.* In this process, the pair of shared electrons which constitutes the hydrogen–oxygen bond in (I) is transferred *in toto* to the oxygen atom in (II); the oxygen atom (1) thus acquires an electron whilst the hydrogen atom (0) loses one.

(ii) *Isomeric change of the enolic ion.* In passing from (II) to (III), the pair of shared electrons which represents the second link of the 2 : 3-double bond is transferred *in toto* to the carbon atom (3), which thus acquires an electron, whilst the carbon atom (2) loses one.

(iii) *Formation of the ketonic ion.* In passing from (III) to (IV), a lone pair of electrons on the oxygen atom (1) is shared with the carbon atom (2) in order to form the second link of the ketonic double bond; in this process the oxygen atom (1) loses an electron and the carbon atom (2) gains one.

(iv) *Formation of the ketone.* Finally, in passing from (IV) to (V), a proton is fixed in the position (4) by sharing a lone pair of electrons belonging to the carbon atom (3); in this case the hydrogen atom (4) gains an electron and the carbon atom (3) loses one.

Each stage in the process is therefore accompanied by the transfer of an electron from left to right, and these four transfers are equivalent to moving a single electron *through the organic compound* from (0) to (4). They thus provide the necessary electrical compensation for the migration of the proton *through the medium* from (0) to (4).

(b) *Characteristics of the Electrolytic Theory of Catalysis.*—(i) The chief novelty of the electrolytic theory consists in the suggestion that isomeric change in the molecule or the ion is effected *by a displacement of valency electrons* between the two alternative points of attachment of the proton, which may be described as the "terminals" of the labile system. Since, however, it has already been pointed out (*Nature*, 1925, **115**, 376) that a mechanism for effecting this flow of electrons is present in all conjugated compounds, it is not

necessary to elaborate this point in connexion with the simpler case of keto–enolic change.

(ii) When compared with the simple ionic theory described above, the electrolytic theory is seen to depend on a *ternary reaction* between the sugar and the acid and basic components of the solvent, whereas Euler postulated a *binary reaction* between the sugar and a catalyst, which may be either acid or basic, but not both. It is, of course, possible that, if the sugar were ionised, say by the removal of a proton with the help of an alkaline catalyst, the resulting anion might be discharged by a proton coming into contact with the opposite " terminal " of the sugar, instead of with the "terminal" from which the proton had been originally removed, thus giving rise to an isomeric form of the sugar; but no provision is made in Euler's theory for any independent supply of protons for this purpose, apart from those which were derived in the first instance from the sugar by ionisation. The electrolytic theory, on the other hand, definitely requires that the medium, instead of being merely an ionising solvent, must be one which can act both as a " proton source " and as a " proton sink."

(iii) A third feature of the electrolytic theory is to be found in the suggestion that the easiest way of effecting isomeric change is to bring the organic compound into a circuit in which it is in contact *simultaneously* with a proton acceptor and a proton donator. It has already been suggested (J., 1925, **127**, 1383, footnote) that the changes in question " may occur simultaneously in the same electric circuit, as in Armstrong's theory of chemical change "; but this tentative suggestion is now advocated as affording for the first time an adequate explanation of the impotence of acids and bases to produce mutarotation when acting alone, and of their wonderful efficiency when acting together. The obvious alternative is to suppose that the acid and basic components of the medium may act on the sugar *consecutively* instead of simultaneously. Thus the action might be supposed to depend on *two consecutive bimolecular actions*, in which the acid and basic components act independently on the sugar (i) to produce a sugar ion by the addition (or removal) of a proton, and (ii) to discharge this ion through the body of the sugar by the removal (or addition) of a proton at the opposite " terminal " of the labile system. The initial stage in this action is, however, an endothermic process, in which the molecules of the sugar are converted into ions of such an unstable character that the dissociation constants are said to be of the order of 10^{-13} and 10^{-19}. The exact amount of energy required to produce these ions is unknown; but it is obvious that, if we can regard the entrance and the exit of the proton as simultaneous, no energy at all is needed beyond the small

amount that is required to cover the difference in energy content of the two isomerides, and perhaps to overcome the "frictional" resistance to the migration of an electron through the sugar. The ternary reaction therefore exhibits, in a characteristic form, the essential feature of a catalysed reaction, since, by making use of a "coupled reaction" in place of two consecutive reactions, it avoids the necessity for lifting the molecule to the high energy level represented by its extremely unstable ions.

Acidity and Basicity as Factors in Catalysis.

In order that the electrolytic theory of catalysis may cover Dawson's experiments, as well as the new results set out in the preceding paper, it is necessary to abandon the narrow definition which measures acidity in terms of hydrogen-ion concentration and basicity in terms of hydroxyl-ion concentration, and to make use of definitions and constants which are not limited to the special case of aqueous solutions. Thus, when water is the solvent, the basicity of a solution can be expressed in terms of its alkalinity, as measured by the concentration of hydroxyl ions in the liquid; but this is no longer true of solutions of nitrogenous bases in non-aqueous solvents, many of which do not contain any oxygen at all. We have, therefore, adopted the more modern view, which regards acidity as a characteristic property of all those hydrogen compounds which can give up a proton to some other molecule or ion, whilst basicity is the more general and passive property of being able to accept a proton from an acid.

(a) *Acid catalysts.* If this conception is adopted we must include as *acids* all those ions or molecules which can give a proton to acetone or to a sugar. Of these acidic catalysts, we may exclude from our consideration the *free hydrogen ion*, $H^{\cdot}$, which is probably non-existent in solution, since its formation can only take place by an endothermic action involving the absorption of about 260,000 calories; it can, however, be replaced (perhaps quantitatively) by the *oxonium ion*, $OH_3^{\cdot}$, which is probably the principal form in which "hydrogen ions" exist in the solution, although the presence of $OH_4^{\cdot\cdot}$ is not excluded. The *undissociated acid*, HX, must also be classed with the oxonium ion as a proton donator, and may therefore be an active catalyst, apart altogether from any pre-existent ionisation, since there is nothing to prevent the molecule of acid from giving a proton directly to the acetone or to the sugar, instead of passing it on (as an oxonium ion) through the agency of a molecule of water; it is also clear that the undissociated molecule of a strong acid is necessarily a more powerful proton donator than the molecule of a weak acid, and must therefore be a much more powerful catalyst,

as Snethlage and others have found to be the case. *Neutral water* also must be classed as a proton donator, quite independently of its pre-existent ionisation, since here again there is no reason why one molecule of water should be compelled to make use of a second molecule of water as an agent for transferring a proton to the ketone or to the sugar.* According to our theory, however, these proton donators can only act in conjunction with a proton acceptor, which in dilute aqueous solutions will usually be a molecule of the solvent.

(b) *Basic catalysts.* Amongst the bases or proton acceptors it is usual to reckon only the *hydroxyl ion* as having any catalytic activity, but for the present purpose the molecule of *neutral water* must also be included as a basic catalyst, in view of the readiness with which it can combine with a proton from the acetone or from the sugar to form an oxonium ion. More novelty is to be found in the perfectly logical conclusion of Brönsted (*Rec. trav. chim.*, 1923, **42**, 718) that *the anion of an acid* is also a base or proton acceptor, in view of the fact that it can combine with a proton to form a molecule of the undissociated acid. The fact that *the basicity of the anion is inversely proportional to the acidity of the acid* provides an obvious explanation of the fact that the chloride ion has no marked catalytic activity, such as is possessed by the acetate ion in virtue of the weakness of the acid from which it is derived. It is of interest to notice that, whilst ammonia is a *base* in virtue of its ability to accept a proton from an acid, the resulting ammonium ion is an *acid* (just like an oxonium ion) in virtue of its ability to give up a proton, *e.g.*, when the ammonium salt is dissociated into the free acid and base, $NH_4Cl \rightleftharpoons NH_3 + HCl$. In the case of ammonium acetate or pyridinium phenoxide, there is a similar reversal of function on the two sides of the equation:

$$\underset{\text{acid}}{CH_3\cdot CO\cdot OH} + \underset{\text{base}}{NH_3} \rightleftharpoons \underset{\text{base}}{CH_3\cdot CO\cdot \bar{O}} \underset{\text{acid}}{\overset{+}{N}H_4}$$

$$\underset{\text{acid}}{C_6H_5\cdot OH} + \underset{\text{base}}{NC_5H_5} \rightleftharpoons \underset{\text{base}}{C_6H_5\cdot \bar{O}} \underset{\text{acid}}{\overset{+}{N}HC_5H_5}$$

On the other hand, a metallic ion, which can neither give nor accept a proton, possesses no acid or basic properties of any kind, and cannot act as a catalyst for mutarotation.

Applications of the Electrolytic Theory of Catalysis.

(a) *The Dual and Quadruple Theories of Acid Catalysis.*—The "dual theory" of acid catalysis met with a good deal of passive resistance merely because it was not easy to see how an acid could

* The ionisation of water cannot give rise to a free proton, and must therefore be written as $2H_2O \rightleftharpoons OH_3^{\cdot} + OH'$, instead of $H_2O \rightleftharpoons H^{\cdot} + OH'$.

act as a catalyst apart from its acidity, *i.e.*, its ability to liberate hydrogen ions. This difficulty no longer exists, however, if we admit that HX and OH_3^+ can both act as proton donators, and so contribute to the catalytic activity of the system, although only the ion is able to contribute directly to its electrical conductivity. Dawson's "quadruple theory" of catalysis presents even greater difficulties, since no hint is given to suggest why the *anions* of a salt should be catalytically active, but not the *kations*. The distinction thus made between anions and kations has, however, been shown to be fictitious, in that it only applies to metallic kations, which cannot take any part in a catalysis which depends on giving or receiving a proton; on the other hand, our own experiments have shown that the ammonium and pyridinium ions, which can give but not receive a proton, both act as catalysts for the mutarotation of a sugar in aqueous solutions. It is also clear that the catalytic activity of an anion depends on the weakness of the acid from which it is derived, and should therefore disappear, as experiment has proved (*e.g.*, in the case of the chlorides), when the anion is derived from a strong mineral acid. If, then, we admit that the kations of a weak base and the anions of a weak acid possess similar catalytic functions to the hydrogen and hydroxyl ions, since they must also be classed as acids and bases in terms of the modern definitions, all the coefficients in Dawson's equation for the catalysis of acetone are then seen to refer to molecules or ions which possess acid or basic functions, thus:

$$v = k_{H}[H^+] + k_a[A^-] + k_{OH}[OH^-] + k_m[HA].$$

On the other hand, those molecules and ions which cannot act as acids or bases are omitted from the equation, since they are not able to influence the course of the change.

(b) *Catalysis by Neutral Water.*—A similar difficulty to that encountered in connexion with the dual theory of acid catalysis is presented by the constant term in Hudson's equation for the velocity of mutarotation of glucose, which we may write as:

$$k_1 + k_2 = 0{\cdot}258[\overset{+}{H}] + 9750[\overset{-}{O}H] + 0{\cdot}0096.$$

The constant term, which accounts for practically the whole of the velocity at the isoelectric point, and for 92% of the velocity in neutral water, was regarded by Kuhn and Jacob as a measure of the velocity of isomeric change in *neutral molecules of sugar*, and by Euler as representing the *isomeric change of a "zwitterion"* derived from the sugar; but it can be explained much more naturally by regarding it as a measure of the catalytic activity of *neutral molecules of water*. It was, however, very difficult to see how water could

act as a catalyst, in a process that is catalysed specifically by acids and alkalis, except by dissociation into hydrogen and hydroxyl ions, the activity of which was already allowed for in the equation. On the other hand, since the electrolytic theory of catalysis postulates that prototropic change depends on the combined action of an acid and a base, we may regard the first two terms in the above equation as representing the combined action of (i) a hydrogen (or oxonium) ion acting as a proton donator at one "terminal" of the sugar, with water as proton acceptor at the other, and (ii) a hydroxyl ion acting as proton acceptor at one "terminal" point with water as proton donator at the other. There is then still room for a "neutral water" term to represent (iii) the action of a molecule of water acting as a proton donator (with formation of a hydroxyl ion) at one terminal, with another molecule of water acting as a proton acceptor (with formation of an oxonium ion) at the other terminal. This neutral-water term, which is independent of the acidity and alkalinity of the solution, does not appear in Dawson's equations, perhaps because the enolisation of acetone is too difficult a process to be effected to any appreciable extent by the combined action of two molecules of water and requires the intervention of at least one component with stronger acid or basic properties. Since, however, components of both types are necessary for the effective catalysis of a prototropic change, all the other terms in his equation must be regarded as representing the combined action of the ions or molecules of the catalyst *with neutral molecules of water*, which would be present in an enormous excess in the dilute aqueous solutions with which he worked.

(c) *Hydrolysis.*—Since the analogy between hydrolysis and prototropic change provided the experimental data from which the mechanism now under discussion was first deduced (J., 1925, **127**, 1379), it is inevitable that the electrolytic theory of mutarotation should be supplemented by an electrolytic theory of hydrolysis. Thus, when regarded from the point of view which is set out above, the rupture of the ester bond in hydrolysis and its formation in esterification are seen to involve a transfer of valency electrons, which is equivalent to the passage of an electric current; the process therefore again resembles an electrolysis of the organic compound between positive and negative poles provided by the acid and basic components of the solution. Whilst, however, any molecule or ion which is capable of accepting a proton from an organic compound can play the part of the base in promoting prototropic change, this is no longer true of hydrolysis, where the *hydroxyl ion* and the *neutral molecule of water* are the only catalysts which are able to provide the necessary atoms of oxygen and hydrogen. We can

therefore foresee that the acetate ion, which has such a marked effect on the mutarotation of glucose, can exert no *direct* action in promoting hydrolysis. Any effects which it can produce must then result from an indirect process of activating either the pre-existing hydroxyl ions or the ester, or (in some more vague way) the medium in which hydrolysis is proceeding. These effects may be purely apocryphal, although they have been used freely to support the view that catalysis by acids depends exclusively on the concentration of pre-existing hydrogen ions. It is, however, noteworthy that, whilst other workers have suspected that the undissociated acid as well as its ions can act as a catalyst in hydrolytic processes such as the inversion of cane sugar, the inherent activity of the anion of a weak acid was only demonstrated when catalysis was studied by a process depending on prototropic change, and not on hydrolysis. Whilst, therefore, it is quite possible that a physico-chemical analysis may disclose some influence of the anion on esterification or hydrolysis, it appears probable that this indirect effect will be very much smaller than the direct effects which have been observed in the iodination of acetone and in the mutarotation of glucose.

Summary.

(*a*) The catalysis by acids and bases of prototropic change and of hydrolysis is interpreted in terms of an electrolytic theory, according to which a flow of valency electrons through the molecule is produced by bringing a proton donator and a proton acceptor, or a hydroxyl donator, into contact with the two terminals of the labile complex.

(*b*) An explanation is given of the parts played in the catalysis of isomeric change by (i) neutral water, (ii) the molecules of a strong acid, (iii) the anions of a weak acid, and (iv) the kations of a weak base. The ineffectiveness of metallic kations in isomeric change and of the anions of an acid in hydrolysis are also accounted for.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, July 28th,* 1927.]

CCCXLI.—*The Quantitative Estimation of Mixtures of Isomeric Unsaturated Compounds. Part II. Iodometric Methods.*

By REGINALD PATRICK LINSTEAD and CECIL JOHN MAY.

RAPID and quantitative addition of halogens to unsaturated substances is known to be prevented if the double bond is in the $\alpha\beta$-position with respect to a negative group. In the case of iodine

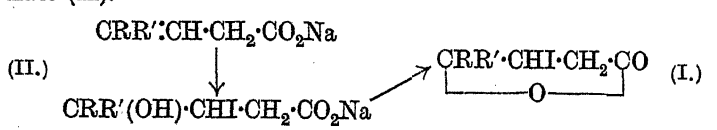
this prevention has been observed with a variety of compounds and is responsible for the low " iodine numbers " sometimes obtained.

For mixtures of isomerides of the type $CHRR_1{\cdot}CH{:}CHX$ ($\alpha\beta$) + $CRR_1{:}CH{\cdot}CH_2X$ ($\beta\gamma$), where X is CO_2H, CO_2R, COR, or other negative group, the velocity of addition of halogen depends on the proportion of the isomerides present, and a bromine addition method for the analysis of such mixtures, based on this principle, has been described (this vol., p. 355). The present communication deals with the application of iodometric methods for the same purpose.

I. *Acids.*

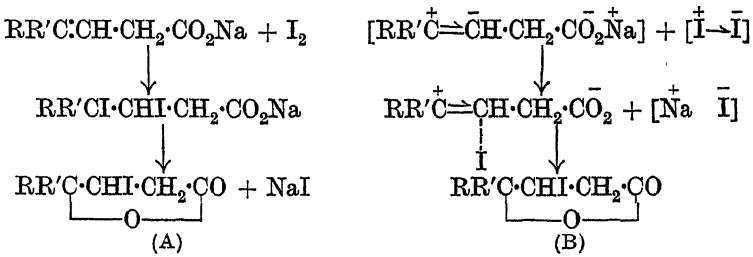
Iodine may be added to unsaturated acids in the form of the chloride (Hübl, Wijs), the bromide (Hanus), or as hypoiodous acid (Margosches, Bougault). In the present work these methods were tested by means of mixtures of two representative unsaturated acids, Δ^1-*cyclo*hexenylacetic acid ($\beta\gamma$) and *cyclo*hexylideneacetic acid ($\alpha\beta$). The $\alpha\beta$-acid showed a much lower reactivity in every case, but the methods did not yield uniformly satisfactory results. Under the conditions of Hübl and of Wijs the end-point in the back titrations was not clearly marked. The use of nascent hypoiodous acid from iodine, moist ether, and mercuric oxide (Bougault) was unsatisfactory for quantitative measurements. The method of Margosches and his collaborators (*Ber.*, 1924, **57**, 996) was of value when a high velocity of reaction was required (see p. 2569). In general, the sodium salt method of Bougault was most satisfactory (*Compt. rend.*, 1904, **139**, 864; *Ann. Chim. Phys.*, 1908, **14**, 145).

Bougault observed that when iodine in aqueous potassium iodide was added to unsaturated acids in sodium bicarbonate solution, $\alpha\beta$-acids were apparently unchanged whilst $\beta\gamma$-acids reacted to give as final products β-iodo-γ-lactones (I). Ponzio and Gastaldi (*Gazzetta*, 1912, **42**, ii, 92) suggested that $\alpha\beta$-acids react extremely slowly under these conditions, and their view has now been confirmed. The difference between the reactivities of the isomerides, however, is large and hence the reaction, as suggested by Bougault, is of value for analytical purposes. According to Bougault the reaction of the $\beta\gamma$-acids takes place by the addition of nascent hypoiodous acid; which must involve the formation of the intermediate (II).



Whilst the present work is not claimed to represent a full study of this reaction, the mechanism suggested above cannot be passed

without comment. In the first place addition of this type would involve an exceptionally high velocity coefficient for the reaction, account being taken of the facts that the formation of lactone is often extremely fast and the concentration of hypoiodous acid in the presence of the excess of sodium bicarbonate is very small (compare Francis, *J. Amer. Chem. Soc.*, 1925, 47, 2340). Again, the sodium salt of a γ-hydroxy-acid such as (II) should show no tendency to lactonise in alkaline solution. We suggest that the mechanism of the reaction is represented either by (A) or by (B), which is a modification of (A) based on the views of Francis (*loc. cit.*) on bromine addition, the first stage being the addition of positive iodine to the negative β-carbon of the ionised salt.*



The velocity of addition *inter alia* would be inversely proportional to the concentration of the salt of the di-iodo-acid (or its ionic equivalent) and would therefore be greatest when this was most rapidly removed as the insoluble lactone. The lack of reactivity of the αβ-acids can thus be attributed in part to the instability of the α-iodo-β-lactones which would be formed as final products. Recent investigations have shown that the presence of two β-substituents has a stabilising influence on the β-lactone ring and facilitates its formation, as anticipated by the Thorpe–Ingold modification of the Baeyer theory (private communication from Mr. S. F. Biggs). It is therefore to be expected that addition of iodine to αβ-acids may be appreciable in the case of ββ-disubstituted acids. We find that with a large excess of iodine under the conditions of Bougault, *cyclo*hexylideneacetic acid gives 32% addition in 24 hours, while with equivalent amounts of reagents the reaction occurs to the extent of some 1% per hour.

The method described by Bougault (*loc. cit.*), which depends on the actual isolation and weighing of unchanged acid (αβ) and of iodo-lactone, gives only approximately correct figures, as it is not possible to obtain complete reaction of the βγ-acid without some conversion of the αβ. In addition, β-iodo-lactones are unsatisfactory substances for quantitative estimation owing to the ease with

* We are indebted to Professor R. Robinson, F.R.S., for this suggestion.

which the iodine atom is displaced by hydroxyl. The following methods of analysis give satisfactory results.

(1) *When the pure isomeric acids are available.* The reaction of iodine with the mixed sodium salts is carried out as described in the experimental portion of this paper. The use of the concentrations suggested by Bougault leads to irregular results and in general the presence of an excess of iodine is detrimental. The most satisfactory results are obtained by using equivalent quantities of $N/20$-iodine and $N/15$-acid (against alkali). A curve connecting composition and percentage addition of iodine is constructed as described in Part I and the compositions of unknown mixtures are found by reference to it. This method is more convenient than that involving bromine addition and the absence of substitution reactions renders it more accurate. The experimental error does not exceed 1%.

(2) *When the isomeric acids cannot be isolated in the pure state.* With certain acids (see *e.g.*, Kon and May, this vol., p. 1549) it is either impossible to obtain definite evidence of homogeneity or else no methods are available for the complete separation of the isomerides, and the interpolation method can no longer be used. In these circumstances the separation method of Bougault has been applied to obtain the value for the position of equilibrium in the *cyclo*heptylideneacetic acids (Kon and May, *loc. cit.*), and the figure so obtained remains to be checked by the more accurate method now available. Attempts were also made to isolate pure di*iso*butylacrylic acid from mixtures by this method, but very little was obtained owing to the velocity of reaction of the αβ-acid with iodine. It has now been found possible to apply a correction for this source of error, which prevents the direct determination of the iodine taken up by the βγ-acid. The extrapolation method described below takes advantage of the *relatively* small reaction of an αβ-acid in mixtures containing its isomeride.

If iodine absorption is plotted against time for a pure βγ-acid, the curve will be that of an ordinary bimolecular reaction, ultimately becoming asymptotic to the line of 100% addition. The curve for the αβ-isomeride will follow the same general course, but over the period during which βγ-addition goes to completion it will approximate to a straight line. For a mixture of the two acids, the curve will resemble that for the pure βγ-acid, but instead of becoming asymptotic to a line parallel to the time axis it will continue along a line representing the αβ-addition after all the βγ-acid has reacted. If, therefore, this rectilinear portion of the curve is continued back to meet the axis, the point of intersection will represent the addition due to the βγ-acid alone. Or, if a_1 and a_2 are the addition values after times t_1 and t_2, then βγ-addition $= a_1 - t_1 (a_2 - a_1)/(t_2 - t_1)$.

It is, of course, only a first approximation to assume that the rate of $\alpha\beta$-addition remains constant during the progress of the $\beta\gamma$-reaction: actually it progressively decreases. The error involved, however, is not large if the conditions of experiment are carefully controlled. To test the accuracy of results so obtained, a series of titrations was carried out with mixtures of Δ^1-*cyclo*hexenyl- and *cyclo*hexylidene-acetic acids of known composition; the curves are shown in Fig. 2.

The strengths of the solutions and the details of the titrations are similar to those described in the experimental portion of this paper for the interpolation method (p. 2573). For a given mixture, four or five determinations of iodine addition must be made at accurately known intervals of time. The following additional features require attention.

(i) In general, the time for complete reaction lies between 2 and 3 hours, provided that the amount of $\beta\gamma$-acid is not above 50% and that the theoretical amount of iodine for 100% addition has been added. Sometimes, however, strict adherence to these conditions makes it necessary to extend the titrations for an inconveniently long time. The period may be shortened by employing an excess of iodine, but this device leads to the occurrence of side reactions. The necessary increase in reaction velocity may be brought about by applying the method of Margosches (*loc. cit.*), which eliminates potassium iodide by using alcoholic solutions of iodine. The retarding influence of potassium iodide on the reaction velocity is clearly shown by the following figures for the reaction with hydrosorbic acid ($CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$): Solutions of 0·0696 g. (0·61 $\times$ 10^{-3} g.-mol.) of the unsaturated acid in 10 c.c. of saturated bicarbonate solution and of 0·1580 g. (0·613 $\times$ 10^{-3} g.-mol.) of iodine in 25 c.c. of 50% ethyl alcohol were added in the order named to 10 c.c. of water containing a definite quantity of potassium iodide. The % reactions were:

KI (g.-mol. $\times$ 10^{-3}) ...	0	0·157	0·314	0·470	0·784	0·941	1·157
% Addition in 10 mins.	54·4	48·2	43·2	40·6	36·2	34·0	32·8

The occurrence of side reactions is not eliminated by this modification, for the curve for the pure $\beta\gamma$-acid shows a noticeable rise above 100% absorption. This does not appear to affect the results appreciably and it would seem that the effects of the side reaction are eliminated by the process of extrapolation employed.

(ii) While it is necessary to use sufficient iodine to ensure the virtual completion *of the* $\beta\gamma$*-reaction* within a reasonable time, any considerable excess over this amount is to be avoided; the amount of iodine used may therefore be reduced below the theoretical quantity for complete reaction of both acids, provided that an

excess of 10—20% above that required for complete $\beta\gamma$-addition is used. The requisite amount can be determined by carrying out a rough preliminary examination of the mixture.

(iii) The most satisfactory method of conducting the experiments is to mix the acid and iodine solutions in bulk and to remove aliquot portions for titration at definite times. This can, however, only be done when the lactone formed is soluble in the particular solution employed. Otherwise there is a tendency for the precipitated lactone to carry down iodine, and it becomes necessary to prepare a number of separate solutions, similar in all respects, each one being titrated as a whole. Iodine occluded in this way does not harm the accuracy of each individual titration, as the lactone is dissolved by the chloroform which is first added.

The application of this method to the determination of the tautomeric equilibria in the dipropyl- and di*iso*butyl-acrylic acids is described on p. 2575.

II. *Neutral Substances.*

The substances examined were ketones and esters, but the methods employed should be applicable to nitriles, substituted esters such as cyano-esters, and probably to olefines containing a phenyl substituent. These compounds were known to add on halogens much more readily than the corresponding acids and it was therefore necessary to find considerably milder reaction conditions. In the first place, the use of bromine in an inert solvent was tried at lower concentrations than those used for the acids (Part I, *loc. cit.*). This work was carried out on the isomeric ketones (III) and (IV) and it was only under extremely mild conditions that the addition to the $\beta\gamma$-ketone (III) was sufficiently slow to be measured. The reference figures for the pure ketones being known, the equilibrium between them was studied:

(III.) $CHMe{:}CEt{\cdot}CH_2{\cdot}COMe \rightleftharpoons CH_2Me{\cdot}CEt{:}CH{\cdot}COMe$ (IV.)

It has been shown (Kon and Linstead, J., 1925, **127**, 815) that this interconversion occurs in cold sodium ethoxide solution, the extent of the change in 28 hours being 15% $\beta\gamma \longrightarrow \alpha\beta$ and 35% $\alpha\beta \longrightarrow \beta\gamma$. It is now found, by the bromine method of analysis, that equilibrium is attained in about 30 hours and is approximately 14% $\alpha\beta$-ketone $\rightleftharpoons$ 86% $\beta\gamma$-ketone. The experimental error, however, is high, at least 2%, and a redetermination by the more accurate iodine chloride method given below has not yet been possible owing to lack of material.

Use of Iodine Chloride.—The well-known Hübl method for the determination of iodine numbers may be modified to give satisfactory results. It has been applied in a number of cases, but only three,

namely, ethyl styrylacetate ($CHPh{:}CH{\cdot}CH_2{\cdot}CO_2Et$), ethyl *cyclo*hexylideneacetate, and ethyl Δ^1-*cyclo*hexenylacetate, will be described. As in the Hübl method, the unsaturated substance or mixture of substances is allowed to react with iodine chloride prepared from mercuric chloride and iodine in alcoholic solution. The concentrations of the reagents are, however, lower than those under Hübl's conditions and the substances are brought together in equivalent amounts. When the pure isomerides are available, an addition curve is constructed in the usual way and the composition of an unknown mixture is determined by reference to it. The experimental procedure for this method is given on p. 2578. In cases where the pure isomerides are not available the extrapolation method already described should be of value; we have, however, not yet tested it.

No evidence of the movement of the double bond in ethyl styrylacetate could be obtained by comparing its iodine figures before and after treatment with sodium ethoxide (compare Linstead and Williams, J., 1926, 2735), for the action of this agent led to partial hydrolysis and partial polymerisation.

Unlike ethyl styrylacetate, ethyl Δ^1-*cyclo*hexenylacetate shows no tendency to condense in the $\alpha\beta$-phase under the conditions of the Michael reaction and therefore it was not expected that sodium ethoxide would cause any tautomeric change in this ester. At 60°, however, the isomeric esters were readily interconvertible and analyses by the iodine chloride method indicated that an equilibrium was reached in the neighbourhood of 10% $\alpha\beta$-ester $\rightleftharpoons$ 90% $\beta\gamma$-ester; the equilibrium mixture derived from the $\alpha\beta$-ester was carefully hydrolysed and substantially pure $\beta\gamma$-acid obtained. The equilibrium figure is close to that (12% $\alpha\beta \rightleftharpoons$ 88% $\beta\gamma$) found for the corresponding acids in caustic alkali solution (Linstead, this vol., p. 2579). It would appear probable that the esters of mono-olefinic acids undergo a reaction analogous to the Fittig change. This does not seem to have been observed previously, although many examples of changes in unsaturated esters containing a second negative group have been recorded (compare Thorpe, J., 1905, **87**, 1670; Vorländer, *Annalen*, 1906, **345**, 244; Farmer, J., 1923, **123**, 3324). This branch of the work is being further investigated.

The iodine chloride addition method has now been used in a study of the pulegone $\rightleftharpoons$ *iso*pulegone change and is being used in that of other tautomeric ketones.

EXPERIMENTAL.

Materials.—The Δ^1-*cyclo*hexenyl- and *cyclo*hexylidene-acetic acids satisfied the usual criteria of purity. The $\beta\beta$-dipropylacrylic acid,

$\beta\beta$-di*iso*butylacrylic acid, and their isomerides were the original materials prepared by Kon and May (*loc. cit.*). The isomeric ethylhexen-β-ones (III and IV) were prepared by Kon and Linstead's method (*loc. cit.*) and had the following properties: $\beta\gamma$-Ketone, b. p. 70°/20 mm.; semicarbazone, m. p. 141° after one crystallisation. $\alpha\beta$-Ketone, b. p. 71°/18 mm.; semicarbazone, m. p. 156° without crystallisation. Ethyl styrylacetate, prepared by esterification of the pure acid, had b. p. 162°/24 mm. This ester underwent slow fission to benzaldehyde on standing and was redistilled immediately before use. Ethyl *cyclo*hexylideneacetate, prepared from the pure acid through the acid chloride (b. p. 104°/11 mm.), had b. p. 111°/16 mm. Ethyl Δ^1-*cyclo*hexenylacetate, made from the pure solid acid through the acid chloride (b. p. 86°/13 mm.), had b. p. 95°/14 mm. The iodine used was of analytical purity.

Reaction of the Isomeric cyclo*Hexenylacetic Acids with Iodine.*—(1) *Qualitative.* Excess of iodine in aqueous potassium iodide was added to a solution of the $\beta\gamma$-acid in aqueous sodium bicarbonate. A resinous oil was formed almost immediately, and after 5 minutes this was extracted with ether; the extract was washed with solutions of sodium thiosulphate and sodium carbonate and dried. The ether was removed cautiously, the last traces in a good vacuum; the residue slowly solidified. Subsequent preparations were readily induced to crystallise by seeding. The crude product was pressed on a porous tile and then boiled in ether with the addition of animal charcoal. The purified lactone, obtained by filtration and evaporation, was recrystallised from light petroleum, the *γ-lactone* of 1-*iodo*-2-*hydroxy*cyclo*hexylacetic acid*, $C_6H_9I<\overset{CH_2}{O}>CO$, separating in white prisms, m. p. 58° (Found: C, 36·0; H, 4·3; I, 46·3. $C_8H_{11}O_2I$ requires C, 36·1; H, 4·2; I, 47·7%). It is soluble in organic solvents except cold light petroleum, insoluble in water and in alkali carbonate solutions, but soluble in caustic alkalis. The crude material has a strong characteristic smell, which is diminished by purification. Hot petroleum solutions develop a characteristic pink colour which is not due to the liberation of iodine. The liquefied lactone decomposes vigorously at 80—100° with the formation of free iodine.

When treated with iodine under similar conditions, the isomeric $\alpha\beta$-acid slowly formed an insoluble resin, which had a strong smell quite different from that of the preceding lactone and could not be obtained in a pure condition. The rate of reaction of the $\alpha\beta$-acid under these conditions was determined in the following experiments.

i. 0·4986 G. of the acid in 25 c.c. of saturated aqueous sodium

bicarbonate was treated with 25 c.c. of iodine solution of Bougault's concentration (25 g. I_2, 40 g. KI, water to 125 c.c.). % Addition found: (in 2 hrs. 10 mins.) 7; (in 24 hrs.) 30, 34.

ii. $0{\cdot}7140 \times 10^{-3}$ G.-mol. of the acid in 10 c.c. of the bicarbonate solution was treated with $0{\cdot}6435 \times 10^{-3}$ g.-mol. of iodine in potassium iodide solution. % Addition found: (in 1 hr.) 1; (in 2 hrs.) 1·9; (in 2 hrs. 30 mins.) 2·7.

(2) *Quantitative.* When mixtures of the acids were treated under the analytical conditions described below, the product was a mixture of the 1-iodo-γ-lactone and the unchanged $\alpha\beta$-acid. The following experiments indicate the degree of completion of the separation. The mixed acids in known proportion (1—2 g.) were dissolved in some 15 c.c. of saturated sodium bicarbonate solution, and iodine (3 g.-atoms to 1 of acid) was added in potassium iodide solution of Bougault's concentration. After 1—2 hours, 4 c.c. of saturated sodium carbonate solution were added and the lactone was isolated in the manner already described. The $\alpha\beta$-acid was separated from the carbonate solution in the usual way and weighed. The weight of $\beta\gamma$-acid present in the mixture was calculated from the weight of crude lactone.

Mixture 1. Found: $\alpha\beta$-acid, 81·8; $\beta\gamma$, 19·6% (= 101·4%). Actual $\alpha\beta$-acid, 85%.

Mixture 2. Found: $\alpha\beta$-acid, 48·5; $\beta\gamma$, 47·7% (= 96·2%) Actual $\alpha\beta$-acid, 52·6%.

Mixture 3. Found: $\alpha\beta$-acid, 80·7; $\beta\gamma$, 24·3% (= 105%). Actual $\alpha\beta$-acid, 76·3%.

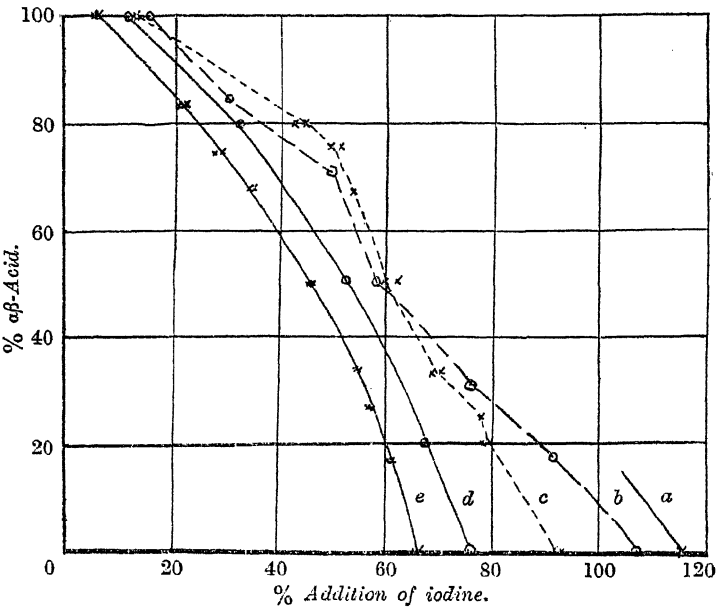
Titration Methods of Analysis.—(1) *By interpolation.* To find the most satisfactory conditions of reaction, various concentrations of the reagents were tried. The results are shown in Fig. 1. Curves *a*, *b*, and *c* were obtained on using 500, 250, and 100% excess of iodine respectively, and curves *d* and *e* on using the reagents in exactly equivalent proportion. The high addition values in series *a* and *b* are due to side reactions still under investigation. Some reaction of the iodine with traces of carbonate present certainly occurs. Curve *e* is the standard reference curve, obtained by using 0·033 g.-mol. of each reagent per litre.

In carrying out a determination, the acid (1/60th g.-mol.) is dissolved in a little saturated sodium bicarbonate solution without heating, and the mixture is then made up to 250 c.c. with the bicarbonate solution. To 10 c.c. of the solution, contained in a stoppered bottle, the theoretical quantity (about 28 c.c.) of approximately $N/20$-iodine (in potassium iodide solution) is added, and the reaction is allowed to proceed for 10 minutes in the dark; 10 c.c. of chloroform and about 200 c.c. of water are then added, the solution

is acidified with hydrochloric acid, and the unchanged iodine immediately titrated with $N/20$-sodium thiosulphate.*

The time of reaction can be altered to bring out the difference in reactivity of any pair of isomerides, provided that the time taken in analyses of unknown mixtures of the isomerides is the same as that taken in the analyses from which the reference curve is constructed. Exact thermostatic control of temperature is unnecessary, but large temperature changes obviously introduce a source of error and are to be avoided.

FIG. 1.



By plotting % addition of iodine against composition a smooth curve is obtained (curve *e*, Fig. 1) which can be used for the analysis of unknown mixtures of these acids.

(2) *By extrapolation.* The titrations were carried out as in the preceding method.

* The acidification is desirable, as traces of carbonate present in the bicarbonate react with hypoiodous acid as follows (Bougault, *Compt. rend.*, 1917, **164**, 949):

$$I_2 + H_2O \rightleftharpoons HIO + HI;\quad 2HIO + Na_2CO_3 \longrightarrow NaIO;$$
$$4NaIO + Na_2S_2O_3 + H_2O \longrightarrow 2NaHSO_4 + 4NaI.$$

The last reaction proceeds concurrently with the ordinary titration reaction and requires only 1/8th of the normal amount of thiosulphate per g.-mol. of free iodine. In the early work described above, this precaution was omitted and there is therefore a slight absolute error.

TABLE I.

Mixtures of Δ^1-*cyclo*Hexenyl- and *cyclo*Hexylidene-acetic Acids.

% $\alpha\beta$-Acid	100	83·7	75·0	66·7
% Addition	5·9, 4·9, 6·3	21·0, 22·4	28·5, 26·8	34·7, 33·3
% $\alpha\beta$-Acid	50	33·3	25·0	16·7
% Addition	43·5, 43·7	53·6, 53·1	56·7, 56·2	60·2, 60·5
% $\alpha\beta$-Acid	0			
% Addition	66·4, 65·5, 65·5			

TABLE II.

Test Mixtures of Δ^1-*cyclo*Hexenyl- and *cyclo*Hexylidene-acetic Acids (see Fig. 2).

Mixture.	Acid in 10 c.c. (g.-mol. × 10^3).	Iodine added (g.-mol. × 10^3).	Iodine solution.	% $\beta\gamma$-Acid. Actual.*	Found.
A	0·7140	0·6435	25 c.c. aq.	0	−0·1
B	0·5897	0·6451	,,	8·7	9·4
C	0·5508	0·6470	,,	23·7	24·7
D	0·7012	0·6451	,,	40·1	40·5
E	0·7226	0·7280	,,	60·9	61·3
F	0·4936	0·5170	15 c.c. alc.	81·4	82·5
G	0·7106	0·8413	32·5 c.c. alc.	100	103

* These points are shown in Fig. 2, marked ⊙, where the ordinates represent % $\beta\gamma$-acid for this purpose.

The iodine solutions in aqueous potassium iodide were similar to those used in the previous method. The solution in alcohol which was used in all the determinations described in this paper had the composition: iodine 6·35 g., 95% ethyl alcohol 600 c.c., water to 1 litre.

The accuracy of the method will not, in most cases, exceed ± 5%, as we consider the *cyclo*hexenylacetic acids to be an exceptionally favourable pair. The method, however, is the only one capable of giving trustworthy results for acids which cannot be completely separated from their isomerides. As such it has been applied in the two cases studied by Kon and May (*loc. cit.*).

Equilibrations.—1. *Dipropyl-acids.* $\beta\beta$-Dipropylacrylic acid and its $\Delta^{\beta\gamma}$-isomeride were heated with aqueous potash under the following conditions:

a.	$\beta\gamma$-Acid	heated	with	excess	60%	potash	for	24 hours.
b.	$\beta\gamma$- ,,	,,	,,	,,	60%	,,	24	,,
			then	with	20%	,,	24	,,
c.	$\alpha\beta$- ,,	,,	,,	,,	60%	,,	48	,,
d.	$\alpha\beta$- ,,	,,	,,	,,	20%	,,	48	,,

The results of iodine absorption by the products (Table III) show that equilibration is slow in 60% potash, probably owing to the sparing solubility of the potassium salts of the acids at this

concentration. The effect on the result of an increase in iodine concentration is shown by the two analyses (cA and cB) of the product in experiment c.

FIG. 2.

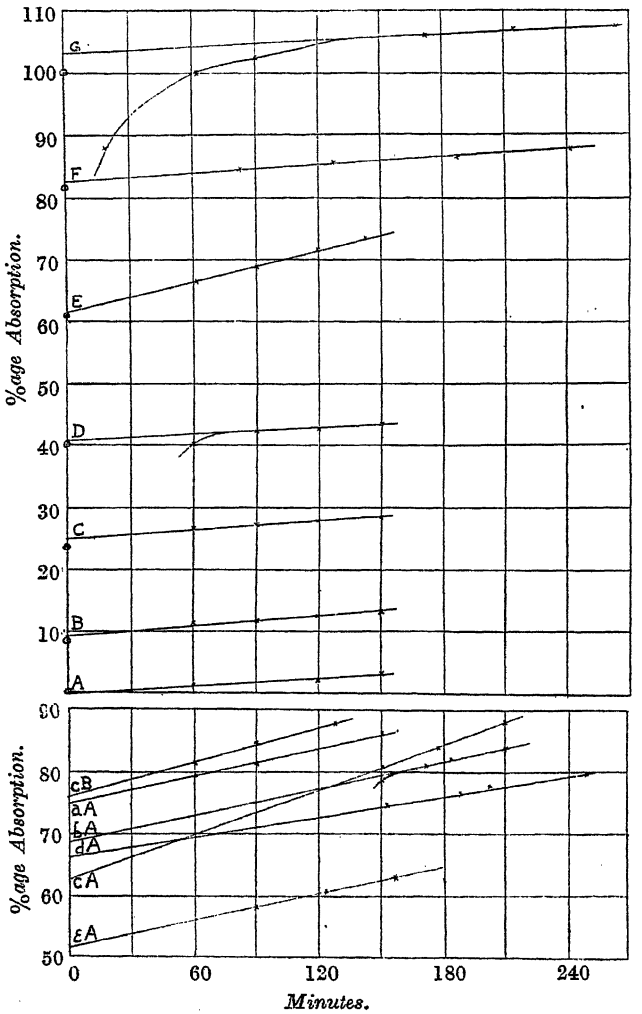


FIG. 3.

2. *Diisobutyl-acids.*—Only one accurate determination has been carried out, on a mixture of ββ-di*iso*butylacrylic acid and its $\Delta^{\beta\gamma}$-isomeride which was heated with 60% potash for 24 hours. The result obtained (51·5% of βγ-acid) by the iodine absorption method

agrees with that to be expected from the physical properties of the mixture (Kon and May, *loc. cit.*).

TABLE III.

ββ-Dipropyl- and ββ-Di*iso*butyl-acrylic Acids (see Fig. 3).

Mixture.	Acid in 10 c.c. (g.-mol. × 10^3).	Iodine in 25 c.c. alcoholic solution (g.-mol. × 10^3).	% βγ-Acid found.
Dipropyl.			
aA	0·5720	0·6182	(74·9)
bA	0·6810	0·6458	68·6
cA	0·6298	0·6458	62·5
cB	0·5530	0·7350	(76·2)
dA	0·4238	0·4125	66·3
			Mean 65·8
Di*iso*butyl.			
eA	0·6380	0·6265	51·5

Addition of Bromine to the Isomeric Ethylhexenones.—The reaction with bromine was studied by the method given in Part I (this vol., p. 355). The reaction of the αβ-ketone with an equimolecular quantity of bromine was approximately bimolecular; the mean velocity coefficients obtained under various conditions are in Table IV, where *c* is the concentration (g.-mol. per l.) of each reagent.

TABLE IV.

Solvent.	*c*.	Temp.	Mean *k*.
CCl_4	1/60	25°	0·0141±0·0059
CS_2	,,	,,	0·0151±0·0094
$CHCl_3$	,,	,,	0·0024±0·0008
$CHCl_3$	,,	0	0·195 ±0·035
CCl_4	1/120	25	0·0052±0·0004

The order for the rates of reaction in the various solvents at 25° is the same as that found by Herz and Mylius for cinnamic acid (*Ber.*, 1906, **39**, 3817), namely, $CS_2 > CCl_4 > CHCl_3$. Under all the above conditions the βγ-ketone reacted completely (within the limits of experimental error).

Experiments at 25° with concentrations of the reagents each 1/300 g.-mol. per litre of carbon tetrachloride (a bromine solution at this dilution retained its strength during the necessary interval of time) showed that the βγ-ketone reacted completely in 6—7 minutes, whereas the reaction of the αβ-ketone was quite slow. The addition figures over a 2-minute interval were determined and compared with those obtained for the equilibrated ketones (prepared in the usual way from the parent ketones by the action of cold sodium ethoxide solution). The figures given in Table V are subject to considerable experimental error owing to the small differences measured.

TABLE V.

Ketone.	Treatment.	Mean % addition of bromine in 2 mins.
$\alpha\beta$	Pure.	37·9 ± 0·6
$\alpha\beta$	NaOEt, 24 hrs.	83·3
$\alpha\beta$	NaOEt, 48 hrs.	89·3
$\beta\gamma$	NaOEt, 48 hrs.	89·2
$\beta\gamma$	Pure.	97·3 ± 1·9

By interpolation the equilibrium is found to be approximately 14% $\alpha\beta$-ketone $\rightleftharpoons$ 86% $\beta\gamma$-ketone. In confirmation, the semicarbazone of the equilibrium mixture was prepared and was found to be mainly that of the $\beta\gamma$-ketone.

Use of Iodine Chloride.—The two standard solutions required in this method contain respectively 3·384 g. of iodine and 5·076 g. of mercuric chloride per 100 c.c. of 95% ethyl alcohol. These solutions are mixed in equal parts 24 hours before use; the mixture does not retain its strength. 10 C.c. are approximately equivalent to 1/1500 g.-mol. of a mono-olefinic substance.

An analysis is carried out by weighing out 1/300 g.-mol. of the unsaturated substance into a graduated flask and dissolving it in 50 c.c. of pure carbon tetrachloride. 10 C.c. of this solution are pipetted into a stoppered bottle. The iodine chloride solution prepared as described above is standardised against $N/20$-sodium thiosulphate and the exact theoretical amount is run into the solution of the unsaturated substance from a burette.* The reaction is allowed to proceed in the dark. At the end of a convenient time, determined by preliminary experiments, the mixture is treated with some 30 c.c. of 10% potassium iodide solution and 300 c.c. of water, and the unchanged iodine chloride is determined by back titration. The isomeric ethyl *cyclo*hexenylacetates showed the expected large difference in reaction; the figures for these esters and for ethyl styrylacetate under these conditions are in Table VI.

TABLE VI.

		Time (mins.).		
		10.	20.	60.
% Addition to ethyl	*cyclo*hexylideneacetate ($\alpha\beta$)	0·2	2·2	4·2
	Δ^1-*cyclo*hexenylacetate ($\beta\gamma$)	56·0, 56·1	62·0	69·8
	styrylacetate ($\beta\gamma$)	34·2	46·4	62·7, 61·8

* If M is the mol. wt. in g. of the substance, t is the titre of 10 c.c. of iodine chloride solution, and F the factor of the thiosulphate (1 c.c. = F g. of iodine), then the volume of iodine chloride solution (J) required by 10 c.c. of a solution containing x g. per 50 c.c. is given by (i) $J = 507{\cdot}6x/MtF$, and the % of unchanged substance at the end of the reaction period by (ii) $1000T/tJ$, where T is the back titre. Expression (i) allows for small discrepancies in weighing the unsaturated material; x/M should equal 1/300 to the nearest milligram.

There was no back reaction with the αβ-ester after titration, but a slow liberation of iodine occurred in the case of the two βγ-esters.

Artificial mixtures of known amounts of the two *cyclo*hexenylacetates reacted as follows in 1 hour :

% αβ-Ester.....	100	75·1	50·2	33·5	25·1	0
% Addition ...	4·2±0·5	23·5±0·05	43·3±0·05	54·5±0·3	59·7	69·8

The smooth composition–addition curve given by these figures was then used to determine the compositions of equilibrated mixtures of the esters. The pure esters were refluxed at 60° with an equimolecular amount of alcoholic sodium ethoxide for 43 hours. The product was in each case poured into water and extracted with ether. After drying and removal of the ether the residue was fractionated. Some 15—20% of liquid was isolated (b. p. 134°/12 mm., probably β-ethoxy-ester), but the bulk of the material was recovered as unsaturated ester, which had the following properties :

Parent ester.	B. p. of product.	% Addition of iodine chloride in 60 mins.	% αβ-Ester (calc.).
αβ	94—102°/12 mm.	68·4 ± 0·1	6
βγ	102—107°/17 mm.	63·8 ± 0·05	16

The equilibrium appears to be of the order of 10% αβ-ester $\rightleftharpoons$ 90% βγ-ester.

The equilibrated ester from the αβ-ester was hydrolysed under conditions precluding isomeric change in the acids, namely, at room temperature with 10% alcoholic-aqueous sodium hydroxide for 4 days. The acid isolated in the usual way was found to consist of Δ^1-*cyclo*hexenylacetic acid [plates, m. p. (crude) 33—34°], contaminated with an oily mixture which deposited more βγ-acid but no αβ-acid on standing.

The authors wish to express their thanks to Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, August 22nd,* 1927.]

CCCXLII.—*The Chemistry of the Three-carbon System. Part XIV. The Effect of Conditions on Isomeric Change in Unsaturated Acids.*

By REGINALD PATRICK LINSTEAD.

IN previous papers of this series the terms "mobility" and "position of equilibrium" were used somewhat freely, but their expression in quantitative terms was not possible. The position

of equilibrium was assumed to be constant for a definite pair of isomerides, and subsequent experimental evidence has supported this view (Linstead, this vol., p. 362; Johnson and Kon, J., 1926, 2748). The work of the latter on the β-alkylcinnamic acids, however, was based on a salt-separation method, whilst that of the present author on the *cyclo*hexane acids was limited in scope. Further work has now been carried out on this important point and on the quantitative expression of mobility. The technique of the equilibration experiments has been improved and the convenient iodine method of analysis (Linstead and May, preceding paper) has been used in place of the bromine method.

The value now found for the equilibrium is 88·2% Δ^1-*cyclo*hexenylacetic acid ($\beta\gamma$) $\rightleftharpoons$ 11·8% *cyclo*hexylideneacetic acid ($\alpha\beta$), which confirms that ($88 \rightleftharpoons 12$) previously reported. The probable accuracy of both analytical methods is shown by the agreement between the results. In addition, it has now been found that this position of equilibrium is, within the limits of experimental error, independent of temperature, concentration of the unsaturated acid and of the catalytic alkali, the nature of the alkali, and the presence of alcohol. It may therefore be regarded with some certainty as a structural constant. The independence of the equilibrium point of temperature indicates that the reaction between the acids, whilst requiring considerable energy for its inception, takes place with scarcely any heat change. In view of the work of Derick (*J. Amer. Chem. Soc.*, 1910, **32**, 1333), it is of interest to note that the ionisation constants of the two acids are very similar, 0·00260 for the $\alpha\beta$- and 0·00249 for the $\beta\gamma$-acid (Zelinski and Izgaryschev, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1379).

The *mobility* of systems such as these, tautomeric in the presence of a powerful catalyst, can only be expressed rationally in terms of the velocity of the interconversion reaction. As previously pointed out (this vol., p. 368), a definite set of conditions has to be standardised before the mobilities of different series can be compared. From a survey of the results so far obtained, the following have been selected as the most convenient conditions : The equilibration is carried out at 100°, the unsaturated acid being treated with 25% aqueous potassium hydroxide (ten times the quantity required for exact neutralisation).* The velocity coefficient of interconversion is given by $k_1 + k_2 = \log_e\{\xi/(\xi - x)\}/t$ (this vol., p. 367). It is proposed to take the expression $100\ (k_1 + k_2)$, when t is expressed

* If 0·01 g.-mol. of unsaturated acid is used, this quantity is 18·12 c.c. of a solution containing 25 g. of potassium hydroxide in 100 g. of solution (30·96 g. in 100 c.c.), $d_4^{15°}$ 1·239. Solutions between 24 and 26%, if used in equivalent amounts, may be taken as satisfactory.

in hours and ξ and x in g. of potassium salt per c.c. of water, as a convenient numerical figure for the *degree of mobility* of the system. For the acids here dealt with, this figure becomes $10{\cdot}0 \pm 1{\cdot}3$ units (see p. 2584). Previous work was not carried out under these standard conditions, but various acids, including the simplest straight-chain olefinic acids, are now being examined with a view to obtain definite values for their mobility and position of equilibrium.

EXPERIMENTAL.

Equilibration.—Δ^1-*cyclo*Hexenylacetic acid and *cyclo*hexylideneacetic acid were prepared and purified by the standard methods. The acid under investigation (1·40 g.; 0·01 g.-mol.) was sealed up in a thick-walled tube of resistance glass with the appropriate amount of alkali. The concentrations and the excess of the alkali solutions were varied to suit the particular conditions required. The concentrations, allowing for neutralisation, of the potassium salt of the acid and the excess alkali in the various solutions are given in Table I.

TABLE I.

Concentrations of Reactants.

	Amount present (g.).			Concentration (g./c.c.).	
Sol.	K salt.	KOH.	Water.	K salt.	KOH.
A	1·78	5·04	15·74	0·114	0·321
B	,,	,,	17·53	0·102	0·287
C	,,	0·56	3·29	0·541	0·170
D	,,	,,	22·63	0·079	0·025
E	,,	,,	13·93	0·128	0·041

Solutions A and B are approximately "standard," the theoretical concentrations conforming with the conditions given on p. 2580 being 0·105 g. K salt and 0·297 g. KOH per c.c.

The reaction tube was heated at the desired temperature in a bath of boiling liquid (chloroform, 61·2°; trichloroethylene, 87°; water, 100°; saturated solution of potassium nitrate, 115°). At the end of the required interval of time the product was freed from a trace of lactone in the usual way and the acid was dried, carefully freed from solvent, and weighed. The loss was of the order of 5%.

Examination of the Mixed Acids.—In the earlier work little or no addition of water to the double bond occurred when the unsaturated acids were boiled with 60% alkali. The absence of such addition products was shown in the present work by the normal iodine addition values of all the products and by the fact that no hydroxy-acid could be isolated by Fittig's method (separation by steam

distillation), although in control experiments a quantity of 2% could readily be isolated under the conditions used.

The mixed unsaturated acids were then examined by the iodine addition method (First method, Linstead and May, *loc. cit.*) and the proportion of the isomerides was determined by reference to the standard curves.

Tabulation and Examination of Results.

I. *Point of Equilibrium.*—

TABLE II.

Concentrations of Reagents—A (Table I).

Expt.	Initial material.	Temp.	Time (hrs.).	Product. % Addition of iodine.	Product. % αβ-Acid.
1	αβ-Acid	100°	21	61·8; 62·8; 62·8; 63·0	12·0 ± 1·0
2	,,	,,	23	63·8; 62·8; 63·2; 62·5	10·8 ± 1·0
3	,,	,,	49	63·7; 62·7; 62·7	10·8 ± 1·1
4	,,	B. p.	7·5	62·6	12·2
5	βγ-Acid	100	8·8	62·6; 62·5; 61·0	13·3 ± 1·7
6	,,	,,	24	62·9	11·0
7	,,	115	17·5	63·2	10·5

The effect of less vigorous conditions was most conveniently tested by starting with the equilibrium mixture. A quantity of this (addition value, 62·6%; αβ-acid content, 12·2%) was prepared from the αβ-acid and treated under the following conditions:

(8) Concentrations, A; temperature, 61°; time, 24 hrs. The product had addition value, 62·5%; αβ-acid content, 12·3%.

(9) 1·40 G. of the equilibrium mixture were treated with 18·62 c.c. of 24·4% KOH solution (B) and an additional 18·62 c.c. of ethyl alcohol were added. Temperature, 100°; time, 24 hrs. The product had addition value, 63·1%; αβ-acid content, 10·5%.

(10) 1·40 G. of the equilibrium mixture were treated with ten times the amount required for neutralisation of a 25% solution of sodium hydroxide. The product had addition value, 61·3%; αβ-acid content, 15·0%.

The mean of these results corresponds to an αβ-acid content at equilibrium of 11·8% ± 1·1%. The corresponding mean value for the equilibrium in boiling 40, 50, and 60% potassium hydroxide solutions is 12% ± 0·8% (Linstead, *loc. cit.*). The equilibrium is therefore constant over a wide range of conditions.

II. *Effect of Temperature on Mobility.*—These experiments were carried out with the "standard" solutions, namely, at concentrations (A). In experiments 18 and 22 the slightly weaker solution (B) was used. The initial material was αβ-acid throughout, except in experiment 28 where βγ-acid was used.

TABLE III.

Interconversion under Standard Conditions.

			Product.		
Expt.	Temp.	Time (hrs.).	% Yield.	% Addition of iodine.	% $\alpha\beta$-Acid.
11	61°	2·0	97	—	100 *
12	„	5·0	97	—	100 *
13	87	5·5	96	16·3; 16·3	90·4
14	„	17·25	90	25·6; 25·2; 25·6	78·7 ± 0·2
15	„	21·0	91	26·5; 24·7; 23·2; 25·0	79·6 ± 1·3
16	„	47·0	97	44·2; 43·5; 43·6	49·7 ± 0·5
17	100	2·0	—	25·1; 23·5	80·3 ± 1·0
18	„	3·92	86	26·8; 26·0	77·5 ± 0·5
19	„	6·0	—	37·8; 37·5; 36·9	60·5 ± 0·5
20	„	6·0	90	34·6; 34·4; 34·9	65·1 ± 0·2
21	„	8·0	94	40·2; 38·8; 38·8; 37·6	58·1 ± 1·2
22	„	8·75	91	43·8; 44·2	49·5 ± 0·5
23	„	10·0	94	47·4; 45·9; 45·5	45·2 ± 1·2
24	„	15·0	89	56·8; 56·3; 54·4	27·4 ± 2·0
25	115	3·08	93	38·9	58·0
26	„	4·5	87	49·5	39·6
27	„	5·5	64	57·3	24·6
28	87	47·0	98	65·3; 64·6; 64·7	5·2 ± 1·1

* From melting point and crystalline form.

The results indicate that there is no interconversion at 61° and that at the higher temperatures the reaction follows fairly closely a reversible unimolecular course. The figures for the velocity coefficient calculated from the equation (p. 2580) are in Table IV.

TABLE IV.

Initial concentration, $\alpha\beta$-K salt 0·114 g./c.c. (except in Expts. 18 and 22); equilibrium concentration of $\beta\gamma$-K salt (ξ) 0·1006 g./c.c.; x = change in concentration of $\alpha\beta$-K salt; t in hours.

	Time.	% $\beta\gamma$-Acid.	x.	$\xi - x$.	$(k_1 + k_2)$.
87°	5·5	9·6	0·0109	0·0897	0·021
	17·25	21·3	0·0243	0·0763	0·016
	21·0	20·4	0·0232	0·0773	0·012
	47·0	50·3	0·0574	0·0433	0·018
					Mean 0·017 ± 0·004
100°	2·0	19·7	0·0225	0·0781	0·126
	3·92	22·5	0·0256	0·0750	0·088
	6·0	39·5	0·0450	0·0556	0·099
	6·0	34·9	0·0398	0·0608	0·083
	8·0	41·9	0·0477	0·0528	0·080
	8·75	50·5	0·0576	0·0430	0·103
	10·0	54·8	0·0625	0·0381	0·097
	15·0	72·6	0·0847	0·0159	0·126
					Mean 0·100 ± 0·013
115°	3·08	42·0	0·0479	0·0527	0·209
	4·50	60·4	0·0689	0·0318	0·256
	5·50	75·4	0·0860	0·0146	0·350
					Mean 0·272 ± 0·051

The reaction velocity is approximately doubled for a 10° rise above 100°, and the low value at 87° is to be expected from the zero reaction at 61°. From the figures found for the reaction at 100°, the degree of mobility of the series is 10·0 ± 1·3. An inspection of the above figures and others previously obtained indicates that for rapid determinations of the degree of mobility of a series it is best to carry out three or four estimations of the amount of interconversion over periods ranging from ¼ to ½ the time required for complete equilibration. On this basis the mobility in the present series would be 9·3 ± 0·8.

III. *Effect of Concentration on Mobility.*—The velocity of the reaction diminishes with dilution and is particularly sensitive to decrease in alkali concentration. The mathematical relationship between these factors has not been obtained, but several points of interest arise from the results given below.

TABLE V.

Initial material, αβ-acid; temperature, 100°.

			Product.		
Expt.	Conc. (see Table I).	Time (hrs.).	% Yield.	% Addition of iodine.	% αβ-Acid.
29	D	21·0	90	21·8; 21·1; 22·0; 19·4	84·4 ± 1·1
30	D	47·5	94	20·2; 18·4	86·7 ± 1·2
31	C	21·0	54	48·1; 48·7; 45·9; 45·6	43·8 ± 2·3
32	E	6·0	94	10·8; 11·8	95·3 ± 0·4
33	E	17·0	97	13·3; 11·9; 15·5	93·1 ± 1·1
34	E	24·0	89	18·2; 15·6; 16·0	89·8 ± 1·2
35	E	41·5	97	20·9; 20·1; 20·9	84·9 ± 0·5

Experiments 29 and 30 show that the αβ-acid is essentially unchanged by 5% alkali just below its boiling point even over long periods of time. In experiment 31, the concentration of potassium salt is very high (five times that under the standard conditions), and the catalyst concentration is about half its standard value. As a result the reaction velocity decreases considerably, there being only 56% change instead of complete equilibration in 21 hours. In the last four experiments (Series E) the concentration of the potassium salt is approximately standard, while that of the catalyst is much lower. The velocity coefficients compare as follows:

	Conc. of K salt.	Conc. of KOH.	Mean $(k_1 + k_2)$.
Standard (Series A)	0·114	0·321	0·100
Series E	0·128	0·041	0·0048

The effect of catalyst concentration is clearly marked. General theoretical considerations indicate that the catalytic agent is the hydroxyl ion and are supported by the fact that sodium hydroxide does not affect the equilibrium attained in potash solution. An obvious analogy exists between this effect and that of the hydrogen

ion in hydrolyses, when the velocity of reaction is proportional to the concentration of the catalyst.

The Hydrolysis of Esters of Mobile Acids.

The results obtained are of value in that they indicate the conditions under which the ester of a comparatively unstable, unsaturated acid can be hydrolysed with alkali without movement of the double bond. The alcohol liberated from the ester does not affect the equilibrium (Experiment 9) and the following results show that, if anything, it has a slight *retarding* influence on the velocity of interconversion.

Concentrations, (A); solvent, 70% water + 30% ethyl alcohol; temperature, 100°.

		Product.	
Time (hrs.).	% Yield.	% Addition of iodine.	% $\alpha\beta$-Acid.
6	96	37·8; 36·4	61·1 ± 1·2
25	94	58·5; 59·3; 57·9; 58·5	21·8 ± 0·9

It may therefore be predicted that in this series hydrolysis of either ester with cold aqueous or alcoholic alkali of any strength will yield the corresponding acid in a state of purity. Hydrolysis with boiling solutions of 10% alkali for periods of 8 hours or so will yield substantially pure products. The latter conditions should prove more convenient than those used at present, which involve 50% alkali and often lead to considerable fission.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CCCXLIII.—*The Chemistry of the Three-carbon System. Part XV. Pulegone and* iso*Pulegone.*

By WILFRED EYNON HUGH, GEORGE ARMAND ROBERT KON, and REGINALD PATRICK LINSTEAD.

THE experiments described in Part X of this series (J., 1926, 3101) made it clear that pulegone (I) and *iso*pulegone (II) were related in the same way as the ketones studied by Kon and Linstead (J., 1925, 127, 815), and that they exhibited what was described as retarded mobility; thus they are quite distinct, but the formation from pulegone of *iso*pulegoneoxime in the presence of alkali (Wallach,

Annalen, 1909, **365**, 240), and of methyl*iso*pulegone by the action of sodium and methyl iodide, on the one hand, and the conversion of *iso*pulegone into pulegone by baryta (Tiemann and Schmidt, *Ber.*, 1897, **30**, 22), on the other, point to the establishment of an equilibrium.

$$CMe_2{:}C\langle \begin{matrix} CO-CH_2 \\ CH_2{\cdot}CH_2 \end{matrix} \rangle CHMe \qquad CH_2{:}CMe{\cdot}CH\langle \begin{matrix} CO-CH_2 \\ CH_2{\cdot}CH_2 \end{matrix} \rangle CHMe$$

(I.) (II.)

Owing to their accessibility, these ketones form a convenient material for the study of tautomerism, but whilst pulegone is well known and readily characterised, the data on *iso*pulegone (especially on its physical properties) are scanty and, in part, conflicting. As a preliminary step, therefore, it appeared necessary to establish definitely the properties of pure *iso*pulegone and to evolve a method of estimating it in mixtures with pulegone.

Probably the simplest method of obtaining *iso*pulegone consists in the preparation of its oxime from pulegone (Wallach, *loc. cit.*), but all our attempts to hydrolyse this oxime led to mixtures containing a high proportion of pulegone and some methyl*cyclo*hexanone.

The ketone is, however, readily obtained by the oxidation of *iso*pulegol (Tiemann and Schmidt, *Ber.*, 1896, **29**, 917), although special precautions are necessary to obtain a pure product (see Experimental). The ketone consists of a mixture of the active and the inactive compound, but in our experiments the latter was only obtained in very small quantities. The optical activity of the active ketone is higher than that previously found.

The method of Harries and Roeder (*Ber.*, 1899, **32**, 3357) is untrustworthy and gives rise to mixtures from which a pure ketone is isolated only with great difficulty; this is *dextrorotatory* and identical with that obtained from *iso*pulegol, as might have been anticipated from the work of Wallach (*loc. cit.*). The lævorotation of the crude ketone is due to the presence of other compounds. The lævorotatory ketone prepared by Grignard (*Compt. rend.*, 1926, **182**, 422) by this method cannot have been *iso*pulegone owing to its totally different physical properties ($d_4^{14°}$ 0·9097, n_D 1·46335); on one occasion we obtained a ketone of very similar properties which consisted mainly of menthone, evidently formed by the reduction of pulegone hydrobromide.

No *iso*pulegone could be found in the three samples of oil of pennyroyal examined. Fractions with properties agreeing with those recorded by Grignard have in every case been isolated, but these consisted mainly of menthone which had already been found

in the oil by Tétry (*Bull. Soc. chim.*, 1902, **27**, 186), a fact which had apparently escaped Grignard's notice. This ketone occurs in a strongly dextrorotatory fraction of the oil, but is, curiously enough, inactive when isolated by means of its semicarbazone. The physical properties of Grignard's natural *iso*pulegone, although almost identical with those of the ketone he prepared by Harries and Roeder's method, differ considerably from those of pure *iso*pulegone; and it appears certain that his material consisted, like ours, of a mixture of pulegone and menthone. It is unfortunate that this material was used by Kon and Nutland (Part X, *loc. cit.*) before its true nature was realised, although the poor yield of methyl*iso*pulegone obtained from "natural *iso*pulegone" was noted at the time. The formation of the methylation product was evidently due to the pulegone still left in the mixture; the methylation has since been repeated with a genuine sample of *iso*pulegone and found to give the same lævorotatory product.

The proportion of pulegone and *iso*pulegone in mixtures of the two ketones can be roughly estimated from the physical properties of the mixture (see Experimental), but a more accurate method has been worked out, based on the different rates of reaction with iodine chloride and similar to that employed by Linstead and May (this vol., p. 2565). This method incidentally provided a ready means of differentiating between *iso*pulegone and mixtures like "natural *iso*pulegone" containing saturated compounds, and supplied the final proof that *iso*pulegone did not occur in the oils examined.

The equilibrium between pulegone and *iso*pulegone was studied in the presence of a variety of reagents with reference both to the rate of equilibration and to the proportion of the constituents in the final product. The results show that the final equilibrium point is so close to pure pulegone that no difference between the latter and the equilibrium mixture can be detected even by the iodometric method employed. The system is evidently very mobile, because in the presence of small quantities of sodium ethoxide (1/50 mol.) the rate of equilibration is already too rapid for exact measurement. With baryta (1/50 mol.) the reaction is complete in 2 hours, but with sodium carbonate it requires several days; piperidine also produces a small change in 24 hours. Cold aqueous sulphuric acid produces little change, but hot acids have a marked effect; this could not be studied quantitatively owing to the ready fission of both pulegone and *iso*pulegone under these conditions, but it is apparent from the fact that, if comparatively large quantities of *iso*pulegonesemicarbazone are hydrolysed by digestion with oxalic acid in a current of steam, the resulting ketone contains up to 50% of pulegone, whereas small quantities can be hydrolysed without

much conversion taking place. The most noteworthy points are the very rapid equilibration in the presence of sodium ethoxide, and the coincidence of the final equilibrium point with pure pulegone, within the limits of experimental error. From these results it is clear that Grignard's figure for the equilibrium between the two ketones (*loc. cit.*) is erroneous; and the great sensitiveness of *iso*pulegone makes its occurrence in essential oils extremely improbable.

EXPERIMENTAL.

Preparation of iso*Pulegone.*—Commercial *iso*pulegol ($\alpha_D^{20°}$ — 1·22°), obtained from Messrs. Boake, Roberts & Co., of Stratford, was oxidised exactly as described by Tiemann and Schmidt (*loc. cit.*), and the resulting oil treated with semicarbazide acetate; the semicarbazone was purified by thorough grinding with light petroleum, followed by repeated grinding with cold ether; the ethereal extract gave on evaporation a solid (E), whilst a large proportion remained undissolved (R).

The solid (E) was freed from adhering oil by means of light petroleum, and a portion was recrystallised from methyl alcohol. The various crops obtained were somewhat indefinite and melted at 157—158°. They were combined and hydrolysed by means of oxalic acid; the ketone had b. p. 94—96°/13 mm., $d_4^{18·3°}$ 0·92540, $n_D^{18·3°}$ 1·47241, α_D + 34·3° (c = 9·1408 in ethyl alcohol),* and evidently contained some pulegone. Another sample obtained in a similar way was treated with aluminium amalgam (Harries and Roeder, *loc. cit.*) before the final distillation; the greater portion had b. p. 100—102°/20 mm., $d_4^{22·0°}$ 0·91759, $n_D^{22·0°}$ 1·46519, $[R_L]_D$ 45·85, α_D + 38·0° (c = 6·6708 in methyl alcohol). The optical activity of the ketone so obtained depends on the number of times the semicarbazone is extracted with ether, the first extract containing the most active material, which is, however, more liable to be impure. Subsequent extracts usually give a semicarbazone which, after several crystallisations from methyl alcohol, forms long, silky needles, m. p. 175—176°.

The residue (R) on crystallisation from methyl alcohol separated in silky needles, m. p. 176—177°, although a small amount representing the least soluble portion formed transparent prisms, m. p. 180°, doubtless belonging to the inactive ketone (compare Wallach, *loc. cit.*); mixtures of the two melted at about 178°. The ketone regenerated from the pure material, m. p. 176—177°, and treated with aluminium amalgam had b. p. 105—106°/23 mm., $d_4^{25·2°}$ 0·91731, $n_D^{25·2°}$ 1·46589, α_D + 23·8° (c = 6·6676 in methyl alcohol), and gave an oxime, m. p. 134° after one crystallisation from methyl

* All the rotations recorded in this paper were measured in a 2-dcm. tube.

alcohol. Another sample similarly obtained from the less soluble portions of (E) had $d_4^{22\cdot5°}$ 0·91994, n_D 1·46689, α_D + 26·6°. When a large quantity of semicarbazone (*e.g.*, 100 g.) was hydrolysed all at once, the product contained as much as 60% of pulegone ($d_4^{18\cdot9°}$ 0·93161, n_D 1·47917); the aluminium-amalgam process of purification is not altogether satisfactory in this case because an appreciable quantity of pulegone is reduced to menthone; but the amount of menthone formed is negligible if the crude *iso*pulegone contains but small quantities of pulegone. For this reason it is necessary to hydrolyse *iso*pulegonesemicarbazone in small portions (about 20 g.). A separate experiment showed that *iso*pulegone was unaffected by treatment with aluminium amalgam, the material having the same physical properties and iodine-absorption before and after treatment (see below).

iso*Pulegone from Pulegone Hydrobromide.*—The preparation was carried out as described by Harries and Roeder (*loc. cit.*). The results were extremely variable, pulegone being usually almost the sole product obtained. This is removed in the process of reduction, but the product then contains menthone; thus, on one occasion a ketone regenerated from the crude semicarbazone had b. p. 84°/9 mm., $d_4^{18\cdot0°}$ 0·90846, $n_D^{18\cdot0°}$ 1·45833, α_D − 11·6°, in good agreement with Grignard's figures (*loc. cit.*); it was reconverted into a semicarbazone from which considerable quantities of menthonesemicarbazone were isolated. In most cases a semicarbazone is formed with great difficulty as already observed by Harries and Roeder (*loc. cit.*). Sometimes, however, almost pure *iso*pulegone is formed; *e.g.*, on one occasion a considerable amount of an optically inactive fraction, b. p. 104—105°/18 mm., was obtained; the refractive index approximated to that of *iso*pulegone, although the density was too high (this was always the case). The product was treated with aluminium amalgam and converted into the semicarbazone. The ketone regenerated from it had b. p. 101—102°/17 mm., $d_4^{20\cdot0°}$ 0·920855, $n_D^{20\cdot0°}$ 1·46669, $[R_L]_D$ 45·81, α_D + 24·7° (*c* = 5·5532 in methyl alcohol), agreeing well with the properties of *iso*pulegone prepared from *iso*pulegol ($d_4^{20\cdot4°}$ 0·92177, $n_D^{20\cdot4°}$ 1·46787). The latter are regarded as the physical constants of the *pure* ketone.

When pulegone hydrobromide was allowed to stand for 4 days with a slight excess of piperidine in light petroleum solution, the resulting ketone proved to be pulegone.

Estimation of Pulegone and iso*Pulegone in Mixtures.*

The proportion of the two ketones in a mixture can be roughly estimated by means of the density or the refractive index, an

examination of several synthetic mixtures having shown that these two properties could be satisfactorily expressed by a straight-line relationship. For the accurate analysis of mixtures, however, the iodometric method of Linstead and May (*loc. cit.*) has been adopted.

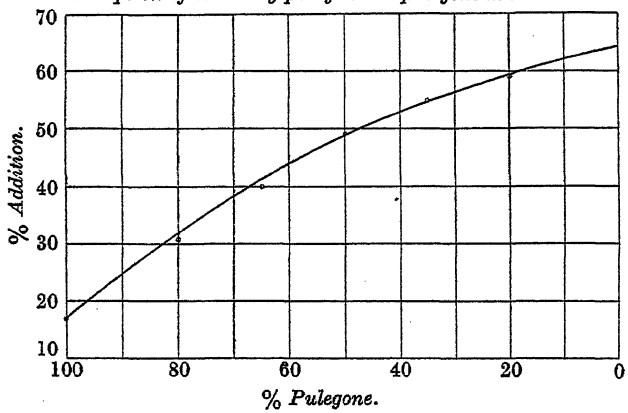
Preliminary experiments were made to ascertain suitable conditions. An *M*/300-solution of each ketone in chloroform was allowed to stand with the theoretical quantity of iodine solution with the following result:

Time (mins.).	2.	10.	20.	27.	
% Reaction with pulegone	5·2	9·9	15·4	—	(complete in 45 hrs.)
,, ,, *iso*pulegone *	32·1	57·5	—	72·6	

* The sample of *iso*pulegone used in the preliminary work was not quite pure.

FIG. 1.

Absorption of iodine by pulegone–isopulegone mixtures.



A standard time of 10 minutes was therefore adopted. Mixtures of pure pulegone and *iso*pulegone, made by mixing *M*/300-solutions in chloroform, were then titrated, with the following results (mean of 3 concordant determinations in each case):

Mixture (% pulegone)	0	20	35	50	65	80	100
% Addition	64·7	58·5	55·1	48·9	40·1	30·9	16·6

From the above data the reference curve (Fig. 1) was constructed.

Examination of Oil of Pennyroyal.

Spanish Oil.—Two samples of this oil gave practically identical results, of which one is recorded: Light green oil, $d_4^{22\cdot5^\circ}$ 0·9324, $\alpha_D^{22\cdot5^\circ}$ approx. + 22°. 1370 G. distilled under reduced pressure (fractionating column) gave:

<92°/11—12 mm.	92—98°/11 mm.	98—105°/11 mm.	Residue.	Loss.
194 g.	1110 g.	7 g.	30 g.	29 g.

The low fraction was refractionated and another large fraction, b. p. 90—91°/10 mm., was obtained, which was increased by a third fractionation. This fraction had $n_D > 1{\cdot}48$ and was therefore added to the main pulegone fraction, which thus amounted to 1270 g., or 93% of the original oil; it had $d_4^{16{\cdot}6°}$ 0·93869, n_D 1·48820; titrations with iodine gave 12·9% addition (mean of 3), showing that no appreciable amount of *iso*pulegone was present. The low fractions gave on refractionation at 10 mm.: 48—52°, 13 g.; 58—62°, 4 g.; 84—90°, 10 g. The terpene fractions were progressively refractionated under atmospheric pressure, but were not definitely separated; a portion, b. p. 168—174°, had $d_4^{14{\cdot}7°}$ 0·85569, $n_D^{14{\cdot}7°}$ 1·46768, α_D — 23° in alcohol; its odour suggested limonene. These were not further investigated. The fraction 84—90°/10 mm. still contained pulegone and terpenes.

750 C.c. of the pulegone fraction were treated with sodium hydrogen sulphite and alcohol until no further precipitation occurred, and the solid was filtered off and washed with alcohol and ether. The oil recovered from the mother-liquor and washings still contained pulegone and was therefore again treated with bisulphite. The portion which had failed to combine was isolated and distilled, but was found to contain pulegone; it was finally reduced by means of aluminium amalgam in ether, and fractionated at 10 mm.:

	Fraction.	Weight.	$d_4^{18°}$.	n_D.
(1)	<83°	3·8 g.	—	—
(2)	83—83	7·9 g.	0·89522	1·45763
(3)	84—87	5·7 g.	0·90822	1·46250
(4)	87—90	6·5 g.	0·91728	1·46669
(5)	High	2·1 g.	—	1·47014

The two lowest fractions were combined and redistilled under ordinary pressure, a part boiling below 200°, and the rest about 207°. The same semicarbazone was obtained from each in moderate yield and melted at 181—182° after washing with petroleum, extraction with ether, and crystallisation from methyl alcohol; this was identified as menthonesemicarbazone (Found: C, 62·5; H, 10·1. . Calc.: C, 62·6; H, 9·9%). The fraction (4), which corresponds with Grignard's *iso*pulegone fraction, had α_D + 43·16° (c = 5·22 in alcohol), and on treatment with semicarbazide gave a sparingly soluble semicarbazone (fine needles from methyl alcohol, m. p. 184—185°) together with a portion which dissolved in ether, from which it was obtained on evaporation as a brown syrup. The ketone regenerated from this by means of oxalic acid was again treated with semicarbazide and gave a product consisting mainly of menthonesemicarbazone. The presence of *iso*pulegone in fraction (4) could not be demonstrated, although its behaviour

towards iodine suggested the presence of some unsaturated material, corresponding with an *iso*pulegone content of 25%. This unsaturated material, however, appeared to be non-ketonic and accumulated in the light-petroleum washings from the menthonesemicarbazone, from which it could be obtained on evaporation; it appeared to be a mixture of menthol and terpenes and was highly unsaturated (iodine number, Hübl: 154·3).

French Oil.—A sample of French oil was found to have properties closely agreeing with those of the Spanish oils: $d_4^{15\cdot9°}$ 0·93671, n_D 1·48627. On distillation, some 1·5% of terpene fraction was isolated; 93% boiled at 98—103°/16 mm. and had $d_4^{15\cdot5°}$ 0·93525, n_D 1·48724; titrations with iodine gave a mean addition of 16%, showing that no appreciable quantity of *iso*pulegone could be present.

The whole of this fraction (839 g.) was treated with sodium hydrogen sulphite for a fortnight, and the oil which had failed to react was isolated and treated again until no further precipitation occurred. The resulting oil amounted to 59 g. and gave the following result on fractionation at 12 mm.:

Fraction.	Weight (g.).	$d_4^{17\cdot7°}$.	$n_D^{17\cdot7°}$.	α_D (in methyl alcohol).
(1) Below 79°	11·3	0·87113	1·45323	+13°
(2) 79—84	4·3			
(3) 84—88	14·9	0·89360	1·45893	+33·0
(4) 88—92	9·2	0·90617	1·46201	
(5) 92—98	4·8	0·91166	1·46728	+29·7
(6) 98—105	4·5	0·91771	1·47309	
Residue	10·0			

Fraction (1) consisted of a mixture of terpenes, whilst fraction (2) contained some menthone; fraction (3) was almost pure menthone, which was also present in most of the other fractions. It was isolated in the form of its semicarbazone, which, after being washed with petroleum, crystallised from alcohol in fine needles, m. p. 184—185°, unaltered on admixture with a sample prepared from *l*-menthone. The regenerated ketone had b. p. 88°/12 mm., $d_4^{19\cdot0°}$ 0·89774, $n_D^{19\cdot0°}$ 1·45233, $[R_L]_D$ 46·35 (Calc., 46·20), but was *inactive*.* Owing to the small amounts of material available it was impossible to decide as to the nature of the menthone originally present, especially as a solid oxime was not obtained; the rotations of the menthone fractions were diminished somewhat by treatment with sodium ethoxide (compare Read and Robertson, J., 1926, 2209). The petroleum washings from the menthonesemicarbazone were evaporated and gave an oil with a strong mint-like odour; on distillation a fraction, b. p. 92—96°/15 mm., was obtained which

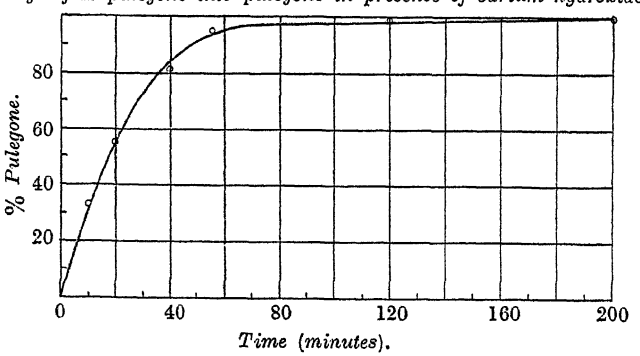
* The hydrolysis of the semicarbazone was carried out with oxalic acid on two separate occasions; the product was inactive in each case.

was probably mainly menthol (Found: C, 76·9; H, 12·3. Calc.: C, 76·9; H, 12·8%), but still contained some unsaturated material; it had α_D + 27·2°, $d_4^{20°}$ 0·89151, n_D 1·45623.

The small fraction (5), which would correspond with Grignard's *iso*pulegone, was specially investigated, but menthone was still the principal constituent, probably accompanied by some pulegone; no trace of *iso*pulegone could be isolated. The slightly high iodine-absorption of the original pulegone fraction is evidently due to the presence of terpenes, which were found to react rapidly with iodine. The terpene fraction obtained in the first fractionation of the oil was feebly lævorotatory (α_D −13·5°), whilst the terpenes isolated from the main fraction were dextrorotatory and had a lower refractive index. The small amounts obtained did not allow of investigation.

FIG. 2.

Change of iso*pulegone into pulegone in presence of barium hydroxide.*



Equilibrium between Pulegone and iso*Pulegone.*—The following procedure was used throughout. The ketone (4 c.c.) was mixed with the catalyst, and the whole made up to 50 c.c. with ethyl alcohol. After standing for the requisite time, the mixture was diluted with water and thoroughly extracted with ether, the extract was washed, dried, and evaporated with the aid of a long column, and the residue was distilled under reduced pressure from a glycerol-bath, the first two drops of distillate being rejected; the remainder was collected (about 3·5 c.c.). The physical properties of the distillate were determined in all cases as an additional check. An *M*/300-solution of the distillate in pure chloroform was then made up and three titrations with iodine were carried out. The catalyst used and its concentration are specified at the head of the corresponding results in the table, and the results with barium hydroxide are illustrated in Fig. 2.

1. *Sodium ethoxide* (10 c.c. of *M*/10-solution).

Initial material.	Time (mins.).	Temp.	*d*.	n_D.	% Addition.
*iso*Pulegone * ...	30	19·0°	0·93448	1·48337	16·9
,, ...	20	19·6	0·93440	1·48483	17·2
Pulegone	720	19·4	0·93599	1·48551	16·6

2. *Barium hydroxide* (10 c.c. of 3% solution).

*iso*Pulegone	10	21·4	0·92540	1·47408	55·2
,, ...	20	21·8	0·92828	1·47751	46·3
,, ...	40	19·0	0·93100	1·48142	30·9
,, ...	55	18·0	0·93251	1·48337	21·0
,, ...	120	19·5	0·93327	1·48483	17·5
,, ...	200	19·6	0·93407	1·48531	17·0
Pulegone	1440	22·6	0·93508	1·48521	16·9

3. *Sodium carbonate* (10 c.c. of *M*/10-solution).

*iso*Pulegone	120	25·0	0·91994	1·47113	58·4
,, ...	900	22·2	0·92419	1·47359	50·4
Pulegone	1440	20·4	0·93506	1·48531	16·9

4. *Piperidine* (10 c.c. of *M*/10-solution).

*iso*Pulegone	1440	20·4	0·92358	1·47408	61·4
Pulegone	1440	21·6	0·93266	1·48483	16·6

5. *Sulphuric acid* (10 c.c. of *M*/10-solution).

*iso*Pulegone † ...	480	22·2	0·92086	1·46966	64·7
,, ...	1440	22·0	0·92092	1·46408	64·7
Pulegone	1440	22·0	0·93508	1·48521	16·6

* In this case 25 c.c. of 12% sodium ethoxide solution were used.
† In this case 10 c.c. of 12·5% sulphuric acid solution were used.

The composition of the mixtures can be readily ascertained from the reference curve in Fig. 1.

The authors' thanks are due to the Government Grant Committee of the Royal Society for a grant which has defrayed the cost of this investigation.

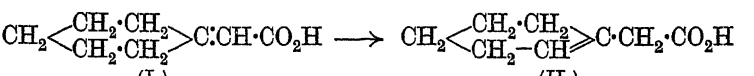
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, July 22nd*, 1927.]

CCCXLIV.—*The Chemistry of the Three-carbon System. Part XVI. The Effect of some Bridged and Unsaturated Rings on Tautomerism.*

By WILFRED EYNON HUGH and GEORGE ARMAND ROBERT KON.

IN several previous papers of this series (J., 1926, 1792, 2727; 1923, 123, 1361, 2440) it has been suggested that the tendency of the double bond to enter a *cyclo*pentane or *cyclo*hexane ring in a com-

pound such as (I) could be correlated with the internal strain in the ring. Particularly striking examples of this correlation were



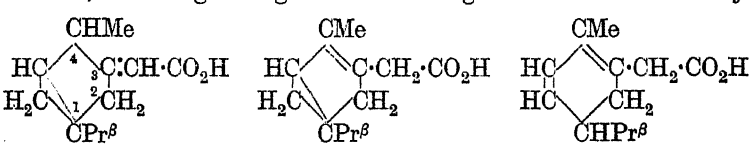
(I.) (II.)

found in ethyl *cyclo*pentylidenemalonate and the *cyclo*hexane compound, the former having the αβ-, and the latter the βγ-unsaturated structure.

In *cyclo*hexane rings which occur in nature the strain is generally relieved either by a double bond (limonene, carvone, piperitone) or by a bridge (thujone, pinene). Such rings, if introduced in place of the simple *cyclo*hexane ring in a compound such as (I), should exhibit less tendency to acquire a double bond and consequently the stability of the βγ-form (II) of the new compounds should be diminished as compared with the acids (I) and (II). The same should be true of compounds in which the *cyclo*pentane or *cyclo*hexane ring already contains a double bond, but the issue here is complicated by the tendency to form a conjugated system with two double bonds in the ring; the βγ-form in these cases should be actually much more stable than in (I) and (II).

In order to test these conclusions, we selected a number of pairs of unsaturated acids containing suitable bridged rings and derived from the corresponding ketones such as β-thujone, pinocamphone, sabinaketone, nopinone, and fenchocamphorone, whilst a variety of acids derived from *cyclo*hexenones had already been prepared by Wallach and were easily available.

β-Thujone was readily converted into the αβ-unsaturated acid (III), but all attempts to prepare the pure βγ-isomeride (IV) * were fruitless, the bridge being attacked to a greater or less extent by

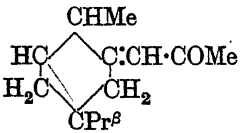


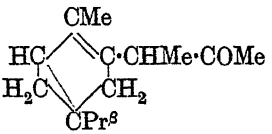
(III.) (IV.) (V.)

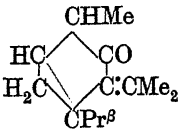
the dehydrating agents employed. The high-melting solid acid so produced evidently contains two double bonds and probably has the structure (V). The αβ-acid, on treatment with alkali, was partly converted into the liquid βγ-isomeride; the equilibrium, estimated by Bougault's method, was 75 : 25 in favour of the βγ-form, as compared with 88 : 12 for the acids (I) and (II) (the method em-

* No attempt has been made to decide between this formula and one with the double bond in the position 2 : 3; the same applies to the compounds (V) and (VII).

ployed gives a *minimum* value for the αβ-acid). The acid (III) can be converted into the corresponding ketone, which, unlike *cyclo*hexenylacetone, has the αβ-structure (VI); it is, however, readily methylated, the new ketone having the βγ-structure (VII). The


(VI.)

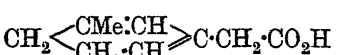

(VII.)

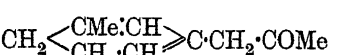

(VIII.)

methylated ketone shows an exaltation of the molecular refraction (0·43 unit), which is, however, less than that of the parent ketone (1·08 units). This is doubtless due to the "conjugation" of the double bond with the three-membered ring in the βγ-formula (VII); the low density of the ketone also supports this formula. β-Thujone readily condenses with acetone, but the product is quite different from the ketone (VI), being a solid of the formula (VIII), having evidently been formed in the same way as the condensation product of acetone and *cyclo*pentanone (Wallach, *Annalen*, 1912, **394**, 376).

These reactions suffice to show that the αβ-form is much more favoured in the compounds derived from thujone than in those derived from *cyclo*hexanone. The reaction with acetone can be taken to indicate that the acidity of the ketone group in thujone is less than that of the ketone group in *cyclo*hexanone, the relatively high acidity of which can in turn be correlated with a tendency to enolisation and thus to the production of a double bond in the ring.

The effect of a bridge containing a carbon atom on the stability of compounds derived from pinocamphone could not be studied, because this ketone, like camphor, could not be condensed either with ethyl cyanoacetate or with ethyl bromoacetate, and we have not yet obtained a sufficient quantity of nopinone or fenchocamphorone to serve as a starting point for further work. In the meantime, it appeared of interest to examine the acid (IX) and the ketone (X) derived from 3-methyl*cyclo*hexenone in which one double bond is already present in the ring.


(IX.)


(X.)

The ester of this acid does not undergo the Michael reaction (Dr. E. H. Farmer, private communication), so evidently it does not possess an αβ-phase. It is now found that the acid itself is unaffected by prolonged boiling with alkali and shows no tendency whatever to pass into its αβ-isomeride. All attempts to synthesise

the latter, and to prepare the ketone from the chloride of the acid, failed.

This behaviour of the acid as a static $\beta\gamma$-form, whilst confirming our view on the probable effect of a double bond in the ring on the stability, is in contrast with that of the cyano-esters prepared by Farmer and Ross (J., 1926, 1570). The reason for the difference appears to be that there are two activating groups in the latter, both favouring the $\alpha\beta$-form and competing with the double bond in the ring, a condition enabling tautomeric equilibrium to be established. In the acid now examined, the stability of one form ($\beta\gamma$) is so much greater than that of the other ($\alpha\beta$) that mobility is completely suppressed. Ethyl α-cyano*cyclo*hexylideneacetate exists apparently only in the $\alpha\beta$-form, whereas Farmer's cyano-esters can be isolated in three forms, of which one is the $\beta\gamma$; the existence of this is evidently due to the additional stabilising effect of the double bond already present in the ring on the $\beta\gamma$-phase.

EXPERIMENTAL.

β-*Thujolacetic Acid.*—β-Thujone was isolated from oil of tansy (Semmler, *Ber.*, 1892, **25**, 3343) and had b. p. 81—82°/12 mm., $d_4^{17\cdot7°}$ 0·91773, $n_D^{17\cdot7°}$ 1·45143, $[\alpha]_D^{17\cdot7°}$ + 75·64°. The semicarbazone crystallised from alcohol in needles, m. p. 174°. The ketone did not condense with ethyl bromoacetate in the presence of magnesium, but the reaction proceeded well with zinc, ethyl thujolacetate, b. p. 136—142°/10 mm., being obtained in 54% yield; much of the ketone was recovered. The acid, m. p. 90—91°, was obtained from it on hydrolysis with sodium ethoxide (Wallach, *Annalen*, 1900, **314**, 166.).

β-*Thujylideneacetic Acid* (III).—The hydroxy-acid was boiled with acetic anhydride for 3 hours and the product was diluted with water and distilled in steam for a long time; the *unsaturated acid*, which separated from the distillate as a solid (yield, 64%), crystallised from light petroleum in needles, m. p. 103—104° (Found: C, 74·2; H, 9·2. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%). On oxidation with alkaline potassium permanganate in a current of steam the acid gave oxalic acid and β-thujone (which was identified by its semicarbazone, m. p. 174°), the structure (III) assigned to the acid thus being confirmed. The *acid chloride*, prepared with the aid of thionyl chloride, had b. p. 136—138°/14 mm.; the *ethyl* ester, prepared by pouring the chloride into ethyl alcohol, had b. p. 136—137°/10 mm., $d_4^{17\cdot8°}$ 0·95995, $n_D^{17\cdot8°}$ 1·47800, $[R_L]_D$ 65·61 (calc., 64·40).* The *anilide* crystallised from petroleum (b. p. 60—80°) in prisms, m. p. 118·5°

* This and subsequent values take into account the exaltation due to the three-membered ring.

(Found: C, 79·9; H, 8·5; N, 5·4. $C_{18}H_{23}ON$ requires C, 80·3; H, 8·6; N, 5·2%).

Dehydration of Ethyl Thujolacetate.—The hydroxy-ester was heated with potassium hydrogen sulphate at 160° for 3 hours, and the resulting ester was isolated by means of steam and distilled. The fraction, b. p. 138—148°/14 mm., was hydrolysed with 30% aqueous potassium hydroxide and alcohol, and the acid formed was liberated and isolated by means of ether. This acid was a mixture of a solid (main product) and an oil. The solid *acid* (V) separated from benzene–petroleum in plates, m. p. 169° (Found: C, 74·2; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%). The oily acid could not be purified and decomposed on distillation, and solid derivatives could not be obtained from it. The same mixture of acids was also produced when the hydroxy-ester was dehydrated with phosphorus oxychloride or pentoxide.

The acid, m. p. 169°, could not be characterised by the formation of derivatives because the acid chloride, although evidently formed, decomposed violently on attempted distillation. The *sodium* salt is characteristic, being sparingly soluble in water and forming fine, silvery plates. The *silver* salt was prepared from it (Found: Ag, 35·9. $C_{12}H_{17}O_2Ag$ requires Ag, 35·9%).

Equilibration Experiments.—β-Thujylideneacetic acid in 1·94 g. lots was heated with 18 c.c. of 25% aqueous potassium hydroxide in sealed tubes at 100° for 24, 32, 40 and 48 hours. The products were worked up under the standard conditions of Linstead and May (this vol., p. 2565) and the iodine values of the equilibrated acids and of the original αβ-acid were then determined as described by them:

Time (hrs.).	0	24	32	40	48
% Absorption	8·4	33·9	52·0	49·6	56·8

The last three values, although not very concordant, suffice to show that equilibration was complete after 32 hours. As the iodine value of the pure βγ-acid was not known, it was necessary to estimate the proportion of the two acids present in the equilibrium mixture by isolating the αβ-acid by Bougault's method (*Ann. Chim. Phys.*, 1908, **14**, 145); this gives the minimum amount of αβ-acid present. For this purpose, 10 g. of pure αβ-acid were heated with potassium hydroxide for 45 hours; the semi-liquid product was isolated as before and treated with iodine under Linstead and May's standard conditions. The excess of iodine was removed with sodium thiosulphate after 10 minutes and the unchanged αβ-acid contained in the aqueous layer was liberated, extracted with ether, and recovered from the extract by evaporation, 2·50 g. being obtained.

This represents a minimum of 25% of αβ-acid in the equilibrium mixture.

The acid (V) was similarly treated with both 25% and 50% potassium hydroxide solution, but in every case it was isolated completely unchanged. The acid was treated with iodine before and after treatment with alkali, and the absorptions were identical within the limits of experimental error (96·1 and 96·3%). The high iodine value and the high melting point (169°) of the acid and its general similarity to dihydro-*m*-tolylacetic acid (see below) point to a formula with two double bonds in the ring. The true βγ-acid (IV) appears to be a liquid.

β-*Thujylideneacetone* (VI).—The chloride of β-thujylideneacetic acid, on treatment with zinc methyl iodide (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 556), gave a 30% yield of the ketone. The sparingly soluble *semicarbazone* crystallised from methyl alcohol in plates, m. p. 191° (Found : C, 67·2; H, 9·2; N, 17·1. $C_{14}H_{23}ON_3$ requires C, 67·5; H, 9·2; N, 16·9%). The *ketone* regenerated from it had b. p. 120°/10 mm., $d_4^{17\cdot4°}$ 0·93111, $n_D^{17\cdot4°}$ 1·48464, $[R_L]_D$ 59·15 (calc., 58·07), its physical properties agreeing with the αβ-structure (VI). The ketone was readily methylated with sodium and methyl iodide (Kon, J., 1926, 1792), a 30% yield of an oil, b. p. 122—124°/14 mm., being obtained. This was converted into the *semicarbazone*, which crystallised from methyl alcohol in plates, m. p. 194° (Found: C, 68·3; H, 9·6; N, 16·1. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·6; N, 16·0%), and was less soluble than the semicarbazone of the parent ketone; a mixture of the two melted at about 176°. The *ketone* (VII) regenerated from the semicarbazone had b. p. 122°/14 mm., $d_4^{17\cdot8°}$ 0·91690, $n_D^{17\cdot8°}$ 1·47339, $[R_L]_D$ 63·12 (calc., 62·69).

Condensation of β-*Thujone with Acetone*.—Dry sodium methoxide, prepared from 12 g. of sodium by Komppa's method (*Annalen*, 1909, **368**, 137), was cooled in ice, an ice-cold mixture of β-thujone and acetone (½ g.-mol. of each) added, and the whole kept in the ice-chest for 4 days. Water and dilute sulphuric acid were then added and the mixture was distilled in steam for a short time. From the residue in the flask a considerable quantity of solid, accompanied by an oil, separated on cooling. The solid consisted of 2-iso*propylidene*-β-*thujone* (VIII) and crystallised from methyl alcohol in needles, m. p. 78·5° (Found : C, 81·2; H, 10·2; *M*, cryoscopic in benzene, 194·6, 186·3. $C_{13}H_{20}O$ requires C, 81·3; H, 10·4%; *M*, 192). Further small quantities of the ketone could be isolated from the oily by-product in the form of its sparingly soluble *semicarbazone*, which crystallised from methyl alcohol in leaflets, m. p. 208° (Found : C, 67·3; H, 9·2; N, 17·0. $C_{14}H_{23}ON_3$ requires C, 67·5; H, 9·2;

N, 16·9%). The ketone, on oxidation with ozone, gave acetone and a substance (giving a purple colour with ferric chloride), which was not further investigated.

Pinocamphone.—This ketone was obtained from oil of hyssop by fractionation under reduced pressure; the fraction, b. p. 84—86°/11 mm., had $d_4^{16\cdot5^\circ}$ 0·95676, $n_D^{16\cdot5^\circ}$ 1·47522, $[R_L]_D$ 44·74, and gave a semicarbazone, m. p. 228°. All attempts to condense the ketone with ethyl bromoacetate, ethyl malonate, ethyl acetoacetate, and ethyl cyanoacetate were fruitless.

*Dihydro-*m*-tolylacetic Acid* (IX).—This acid was prepared from 3-methyl*cyclo*hexenone as described by Wallach (*Annalen*, 1902, **323**, 138). The pure acid was treated with potassium hydroxide as described on p. 2598, but was recovered completely unchanged. Specimens of the acid before and after treatment with alkali were treated with iodine, but no difference in iodine absorption could be detected (95·6% in both cases).

Attempts to prepare the corresponding ketone (X) by the Blaise–Maire reaction failed because the chloride of the acid, like that of the acid (V), could not be distilled. The crude acid chloride did not give a satisfactory product.

Attempts were also made to obtain the ketone by condensing 3-methyl*cyclo*hexenone with acetone, but a pure substance could not be isolated from the complex mixture formed.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CCCXLV.—*The Constitution of Colloidal Platinum.*

By STUART W. PENNYCUICK.

THE source of the charge on colloidal metal particles, as prepared by the Bredig sparking method, has been a debatable question for many years. The older ideas, that the electrical method was one purely of dispersion and that the charge was frictional, have been shown to be insufficient and incorrect. At present two opposing views stand out. Both agree that the charge is ionic, and also that the method of preparation consists essentially in a mechanical dispersion to a vapour of perhaps atomic dimensions, with a subsequent condensation to form the colloid particles. They differ, however, as to the source of charge. One holds that the charge is

due to the combination of the condensed particles with certain foreign ions present in the medium. The other claims that the mechanical dispersion is always accompanied by the oxidation of the metal, and that in the subsequent condensation the fine particles of metallic oxide combine or react with the water to form a complex kation (in the case of copper or silver), or a complex anion (in the case of gold) (see Wo. Pauli, *Trans. Faraday Soc.*, 1921, **16**, 14; Fuchs and Pauli, *Koll.-Chem. Beih.*, 1925, **21**, 195; Paine, *ibid.*, 1912, **4**, 24; Rebière, *Compt. rend.*, 1912, **154**, 1540; Beans and Eastlack, *J. Amer. Chem. Soc.*, 1915, **37**, 2667).

The former explanation is the one more generally accepted, but it is shown in this paper that in the case of colloidal platinum, at least, although it may be difficult to fix the structure of the complex platinum anion, nevertheless the latter explanation appears to be the correct one. It will be shown that colloidal platinum solutions can be prepared of such strengths that their high conductivities cannot possibly be due to the impurities present, and further that all such solutions are definitely acid.

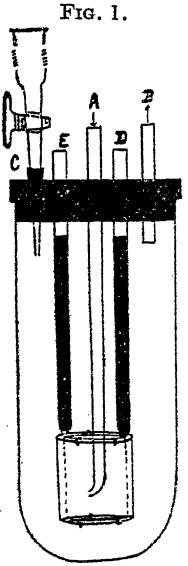
The Preparation of the Platinum Sols.—It is well known that platinum sols can be prepared in the total absence of added stabilisers, and accordingly those used throughout this work were prepared by sparking pure platinum electrodes in conductivity water and in the absence of carbon dioxide. The conductivity-water still was after the design of Bourdillon (J., 1913, **103**, 791), and the water used had a specific conductivity of 0·2—0·4 gemmho at 18°. The sparking apparatus was the same as that described by Pennycuick (*Australian J. Exp. Biology*, 1927, **4**, 99). Briefly, it consisted of a short-necked 500 c.c. borosilicate flask, through the cork of which two platinum electrodes passed to a small ebonite frame above. One electrode was firmly fixed whilst the other had a small range of vertical freedom. This freedom was used to close the spark gap, and a spiral spring on the movable electrode threw the gap open to any prearranged extent. The cork also carried an inlet and an outlet tube, so that during the preparation carbon dioxide-free air could be slowly bubbled through the sol. These tubes also served for the introduction of the conductivity water and for the removal of the prepared sol. All the connexions through the cork were air-tight, and the method of preparation therefore precluded the accidental introduction of any impurities.

It was essential to make certain that the only foreign matter present was that which was initially in the conductivity water, and this was kept strictly in mind. The air used was in every case freed from carbon dioxide. The conductivity water under air pressure was siphoned into the sparking vessel until a sample

from the latter showed a specific conductivity of less than 0·4 gemmho. About 450 c.c. of platinum sol were prepared at each operation, and during the sparking the sample was kept very close to 0° by the use of a freezing mixture. A direct current of about 5—6 amps. was used at 220 volts, and the time of sparking (excluding stoppages) was approximately 18—20 minutes per 450 c.c. of water.

The Conductivity Cell.—The conductivity cell was very similar in design to that used by Beans and Eastlack (*loc. cit.*). It was of borosilicate glass and had a total capacity of 120 c.c. The cell constant was 0·0107. The cell mouth was fairly wide (38 mm. diameter) and ground, and was closed with an ebonite stopper surrounded with an air-tight rubber band. The stopper carried 5 tubes (see Fig. 1)—the two electrode tubes D and E, an inlet and an outlet tube for air-stirring, A and B, and a spare tube for the introduction of any solution. All tubes were firmly fixed, and when in use the cell was air-tight. (I am indebted to Mr. J. S. Walker, B.Sc., for this cell, which proved very satisfactory.) All conductivities were measured in an electrically controlled thermostat at 25°.

FIG. 1.



The Specific Conductivity of the Platinum Sols.—Particular care was taken to keep the platinum sols pure. After preparation they were siphoned under air pressure, into thoroughly cleaned borosilicate flasks, always in the absence of carbon dioxide. They were kept for several days in order to allow the layer particles to precipitate, and the overlying sol was then siphoned into stock flasks and kept at the required temperature until wanted, the necessary quantity then being siphoned into the conductivity cell. The many samples examined are believed to be quite free from contaminations, including atmospheric carbon dioxide.

The first interesting point noticed was that the sols which had been prepared and stored at 0°, when put in the bath and allowed to come to 25°, showed a steady increase in conductivity over several days. Examples of such changes (at 25° and at 30°) are set out in Table I A.

TABLE I A.

Time interval (hrs.)	0	½	2	4	8	16	24	36	∝
κ (gemmhos) (at 25°)	5·65	6·10	6·58	7·05	7·97	9·23	9·91	10·42	14·3
κ (gemmhos) (at 30°)	5·68	6·96	8·20	9·02	10·00	11·17	11·69	12·01	14·6

An attempt was made to determine whether these changes followed any known velocity law, and, if possible, to obtain the temperature coefficient of the action; but although all solutions showed the same general changes, different samples of the same solution gave curves which did not correspond. (This is yet another example of the difficulty of reproducing exactly the same conditions in two samples of a colloidal solution.) All that could be concluded was that the change was always very rapid initially and then progressively slowed down.

The figures in Table I A, and in fact all similar figures, indicated that the specific conductivities of the platinum sols were approaching some limiting equilibrium value. Accordingly the solutions were boiled for 3 minutes and the conductivities redetermined, and it was thus found that equilibria were practically reached at 14·3 and 14·6 gemmhos in the above cases. It was observed that these values with the boiled solutions were not set up at once, but that the conductivities again changed with time. With these sols, however, the conductivities decreased, but the change was far less than before. Further investigation of the boiled and stable sols then revealed that, after any temperature changes, there was a lag in the equilibrium as indicated by conductivity measurements; a hot sample cooled to 25° always showed a steady fall in conductivity, whilst a cold sample warmed to 25° showed a corresponding rise, such changes being measurable over several days. These conclusions have an important bearing on the later work in this paper. The abnormally large lag shown by the unboiled solutions which had been made and kept at 0° (see Table I A) seems to indicate that these solutions have never reached their equilibrium; and this is supported by the fact that the unboiled platinum sols kept and *measured* at 0°, did not reach a maximum conductivity value even after 2 months.

Beans and Eastlack (*loc. cit.*), starting with conductivity water of 0·8 gemmho, prepared platinum sols of $\kappa = 3{\cdot}5$—$4{\cdot}3$ gemmhos. Further, they showed that the specific conductivity due to the charged platinum particles, calculated from their number, their charge, and their mobility, was of the order 0·0001 gemmho, and therefore negligible. They concluded that the "mechanical dispersion of the metal was followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium." The present work goes considerably further, for, by starting with conductivity water of a maximum conductivity of 0·4 gemmho, and taking special precautions to exclude contaminations, platinum sols were readily prepared with specific conductivities which rose to 14·6 gemmhos. Further, as there was

no reason to believe that this was a limiting value, stronger sols were prepared by prolonged sparking which gave specific conductivities (after boiling) as high as 16·8 gemmhos. Higher values could probably have been obtained but prolonged sparking caused abnormal platinum wastage. Higher values were actually obtained by the prolonged boiling of a platinum sol, and also of course by evaporation; *e.g.*, an unboiled sample of $\kappa = 6{\cdot}21$ was boiled in a Pyrex flask in contact with carbon dioxide-free air; after 5 minutes' boiling it rose to 12·76 and after 25 minutes to 21·46 (all readings being taken at 25°). Conductivity water, when treated in the same flask in the same way, showed a change of κ from 0·4 to 0·89 gemmho. Similar platinum sols, when boiled in a large platinum dish for 2 minutes and for 15 minutes, showed $\kappa = 15{\cdot}35$ and 41·2, respectively; evaporation probably accounted for the latter high value. The highest conductivity obtained for a platinum sol by boiling in a platinum dish was 66·1 gemmhos. It was found that these high values very slowly decreased when the sol was kept at 25° for several days, but the fact that such values are actually obtained is very interesting. It is quite impossible, in view of the experimental precautions, to imagine that these conductivities can be due to the impurities present. The alternative, and the only reasonable explanation, seems to be that an electrolyte is formed during the sparking process.

Now it is well known that colloidal platinum particles carry a negative charge; and as a working hypothesis, the author suggests, in conformity with the theory of Pauli (see Pauli and Perlak, *loc. cit.*), that during the disintegration process some of the platinum is oxidised, and that during the subsequent condensation some platinum particles and some oxidised platinum particles coalesce; the oxidised platinum, however, in contact with water acts as an electrolyte (probably H_4PtO_4), with the result that the growing platinum particles form a complex anion, or ionic micelle of structure $[Pt_x(PtO_4)_y]^n$, which is in equilibrium with an equivalent amount of hydrogen ions. The high conductivities obtainable indicate that at least a small proportion of the hydrogen ions are "free," *i.e.*, that some of the complex is wholly ionised; whilst the lag in the equilibrium which is always shown when the sol suffers a temperature change, indicates that some of the hydrogen ions are held at the surface or in a surface double layer, and that rearrangements are slow and probably complex. These slow rearrangements are probably related to the slow equilibria changes in colloid systems observed by Du Noüy ("Surface Equilibria of Organic and Biological Colloids," 1926, p. 155).

It now remains to be shown that the complex anions and the

corresponding hydrogen ions are actually present. With regard to the former, all that can be said at present is that it has been abundantly proved that the platinum particles in the absence of foreign electrolytes are negatively charged, but the exact constitution of the micelle is so far unknown. With regard to the hydrogen ions, however, definite evidence will now be produced which clearly indicates the existence in the pure platinum sol of "free" hydrogen ions and also of slowly removable hydrogen ions, the latter being probably on the micelle surface or in the double layer.

The Titration of Platinum Sols.—Having obtained platinum sols of remarkably high specific conductivities, and believing that the charged platinum anions contributed only a negligible fraction thereof, it was considered that any real existence of hydrogen ions would be revealed by the titration of the sol with a base. For this purpose, the cell already described was utilised; 60 c.c. of the platinum sol were carefully introduced into the cell, and put into the bath at 25° until equilibrium was attained, or until the conductivity showed a negligibly small change over a period of 1 hour. A 3 c.c. burette, containing the titrating base and with a soda-lime tube on the upper end, was introduced into the opening C. A piece of rubber tubing on the lower end of the burette ensured an air-tight connexion; air was bubbled through a wash-bottle in the bath, containing a corresponding sample of the sol, and then through A into the cell for the purpose of efficient stirring and mixing. The exit tube B was connected to a water trap. Titrations were carried out initially with sodium or potassium hydroxide. These bases were prepared with conductivity water, diluted to exactly 0·001*N*, and stored in waxed bottles. They were introduced into the pipette without coming in contact with the air.

Now, if practically the whole of the conductivity of the platinum sol be due to the hydrogen ions, then from the known mobility of the hydrogen ion at 25° one may calculate at once its concentration. Writing the equivalent conductivity as equal to the sum of the ionic conductivities, we have

$$\Lambda_v = \Lambda_{H^+} + \Lambda_{Pt\ complex^-};$$

and neglecting the last term,

$$\Lambda_v = \Lambda_{H^+} = 349{\cdot}5,$$

whence $\kappa v = 349{\cdot}5$, where κ is the specific conductivity, and v is the volume in c.c. containing 1 g.-equiv. of hydrogen ions. We have then $v = 349{\cdot}5/\kappa$, and therefore $1000/v$, or the normality in the usual units, is given by $\kappa/0{\cdot}3495 = \kappa$ in gemmhos/349,500. (The ionic mobilities in this paper are calculated from those at 18°

by the use of the corresponding temperature coefficients; see H. S. Taylor, "A Treatise on Physical Chemistry," 1924, p. 540.)

Every platinum sol titrated showed with all bases used a minimum in the titration curve, indicating very clearly the presence of an acid or of titratable hydrogen ions—acids and salts showed no such minima. Further, with sodium and potassium hydroxides, all the platinum sols of various strengths showed a very good agreement between the hydrogen-ion concentration as calculated above from direct conductivity and that obtained from the minimum on the titration curve. Several normal cases are set out in Table I B. The differences in the minima shown by the two hydroxides are negligible.

TABLE I B.

	1.	2.	3.	4.	5.	6.	7.
κ (gemmhos)	6·57	7·00	12·76	15·03	15·35	21·46	41·2
(A) Normality of H^+ (calculated from κ) $\times 10^6$ ...	19	20	36	43	44	61	120
(B) Normality of H^+ (by titration) $\times 10^6$.	17	16	37	44	45	65	140

The normality marked (A) is calculated from κ (gemmhos)/349,500; that marked (B) is the normality of the solution with regard to total alkali hydroxide at the minimum on the titration curve. The figures in cols. 1 and 2 are for two unboiled samples. As such samples are not in equilibrium they were titrated fairly rapidly and the titration minima are approximate only. The figures in cols. 3, 4, and 5 are for samples which were brought to equilibrium by boiling for 2—5 minutes. Cols. 6 and 7 relate to samples boiled in Pyrex for 25 minutes, and in an open platinum dish for 15 minutes, respectively. They titrate fairly well.

From the agreement between the figures in Table I B, three conclusions may be drawn: (*a*) Colloidal platinum sols are definitely acid; (*b*) practically the whole of their conductivities can be attributed to the hydrogen ions present (the complex anion having negligible mobility); and (*c*) platinum sols behave as strong acids, for only strong acids show the correct conductivity minima when titrated with alkali hydroxides (see Eastman, *J. Amer. Chem. Soc.*, 1925, **47**, 332). A more detailed consideration, however, indicates that whilst the first of these conclusions is undoubtedly correct, the second and third cannot both be true. Table II shows the figures obtained on titrating platinum sols with each alkali, and also those obtained by titrating hydrochloric acid with potassium hydroxide. The latter figures allow a comparison to be made between the platinum sol and a strong acid, and they serve also to show that certain irregularities in the platinum sol titration curves

are not inherently due to the abnormally small concentrations with which we are here dealing (*q. v.*).

TABLE II.

Titration of platinum sols.				Titration of 0·04446*N*-HCl.	
With KOH.		With NaOH.		With KOH.	
Normality × 10^7.	κ.	Normality × 10^7.	κ.	Normality × 10^7.	κ.
—	15·14	—	15·03	—	18·65
123	12·05	79	12·55	62	16·90
228	9·62	164	10·38	151	14·44
307	8·10	276	7·73	236	12·12
400	7·14	415	6·04	340	9·34
476	7·18	536	6·46	420	7·54
566	7·80	625	7·24	463	7·35
669	8·67	741	8·84	504	7·88
783	10·17	826	10·14	583	9·43
895	12·05	937	12·03	828	14·92
1004	13·82	1045	13·80	963	17·86

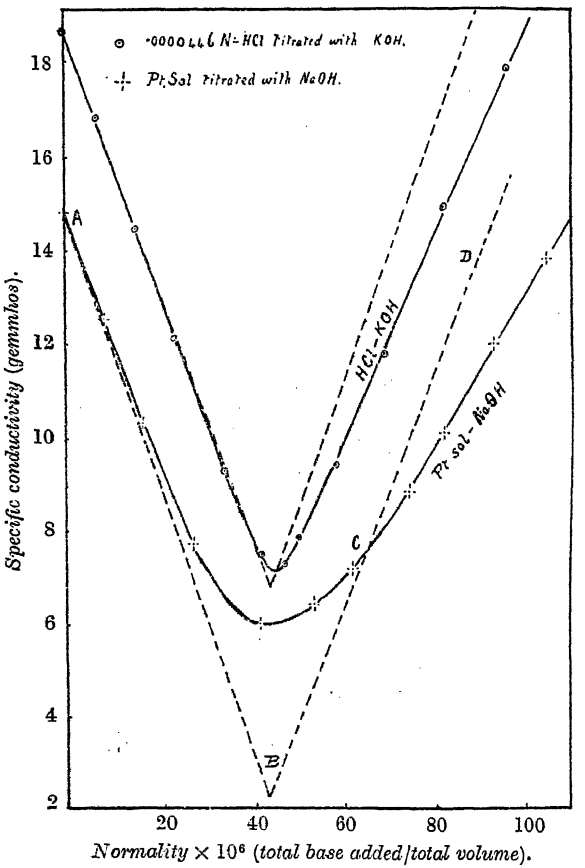
The normality refers to that of the solution in respect to total sodium or potassium ions present, and is the quotient Total base added/Total volume of solution.

The corresponding curves are shown in Fig. 2. The KOH–Pt sol curve is omitted, because it is of exactly the same form as the NaOH–Pt sol curve; in fact, the differences between the two curves agree remarkably well with the calculated differences between the mobilities of the potassium and sodium ions. This is also the case with the corresponding hydrochloric acid–strong base curves. Accordingly only the two curves shown in Fig. 2 need be discussed.

The initial specific conductivity of the platinum sol was 15·03 gemmhos, which, on the assumption that the hydrogen ion is practically the sole contributor to the conductivity, represents a hydrogen-ion concentration of 43×10^{-6}. The minimum on the curve appears to lie between 42×10^{-6} and 44×10^{-6}. At this minimum, the corresponding specific conductivity of the solution is 6 gemmhos; but if the platinum sol is behaving as a strong acid, then the minimum point on the curve will indicate that the whole of the hydrogen ions have been replaced by sodium ions, and the specific conductivity of 43×10^{-6} equivs. of sodium ion is only 2·27 gemmhos. The broken-line curve, ABCD on the figure, is that calculated from the mobilities of hydrogen, sodium, and hydroxyl ions on the foregoing assumptions. Although the curves are similar in shape and situation, the divergence is pronounced. In order to see whether titrations at such low concentrations were trustworthy, hydrochloric acid of approximately the same normality (*viz.*, $44{\cdot}6 \times 10^{-6}$) was titrated with various bases, and the HCl–NaOH curve also appears in Fig. 2. Other and weaker hydrochloric acid solutions were similarly titrated, and in every case the theoretical

and experimental end-points showed remarkably good agreement. In the curve illustrated, the end point corresponds to a concentration 45×10^{-6}, and the broken-line curve is the corresponding theoretical curve calculated from mobilities. The close approximation of the turning points in these two curves (Found: $\kappa = 7{\cdot}18$. Calc.: $\kappa = 6{\cdot}81$) shows that such titrations are quite trustworthy; and

FIG. 2.

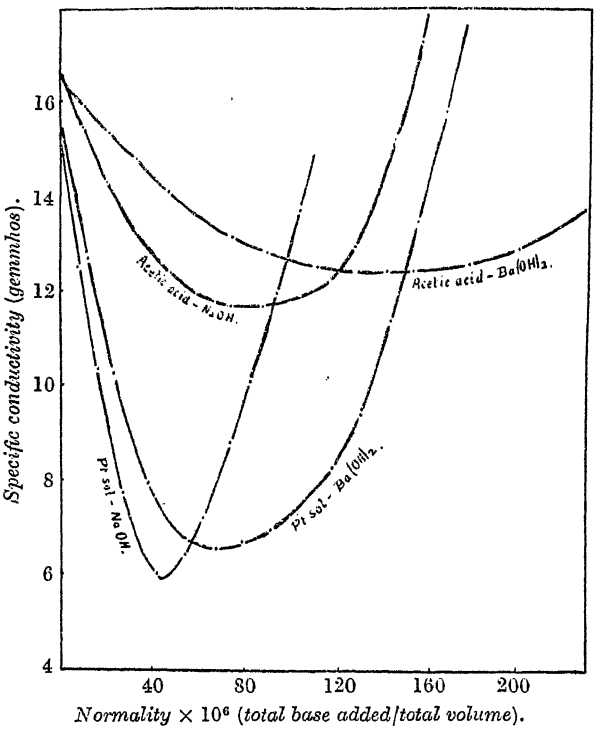


the divergence of the two curves after the turning point is doubtless due to the mutual repression of ionisation of the sodium chloride and hydroxide present.

Returning then to the platinum sol titration curve, the difference between the specific conductivities at the experimental minimum (6 gemmhos) and at the theoretical minimum (2·27 gemmhos) needs

explanation. It appears either that some of the conductivity of the sol is contributed by other than the hydrogen ions, or that the colloidal platinum does not function as a strong acid. If either of these suggestions be true, then the agreement between the concentrations set out in Table I B would appear to be largely fortuitous This may actually be the case, for although a wide range of platinum sols was taken, the titrating bases were chemically similar. Accordingly, the titrations were repeated with calcium and barium

FIG. 3.



hydroxides, both prepared with the usual precautions and diluted with conductivity water to 0·001*N*. The two curves differed only slightly, and the difference could be directly ascribed to the difference in the mobilities of the barium and the calcium ions. Accordingly, Table III and Fig. 3 contain the details for only one of these bases. As a titration curve for a weak acid is also necessary for comparison, Table III and Fig. 3 contain the details of the titration of acetic acid of comparable conductivity (0·000141*N*) with sodium and calcium hydroxides.

TABLE III.

Titration of Pt sol with $Ba(OH)_2$.		Titration of 0·000141*N*-acetic acid with NaOH.		with $Ba(OH)_2$.	
Normality $\times 10^6$.	κ.	Normality $\times 10^6$.	κ.	Normality $\times 10^6$.	κ.
—	15·40	—	16·56	—	16·48
11·9	12·71	9·8	15·44	11·2	15·88
23·7	10·28	20·4	14·31	21·4	15·32
38·1	7·98	33·0	13·28	32·9	14·74
55·7	6·69	47·3	12·44	46·8	14·11
68·0	6·59	58·1	12·03	75·3	13·25
79·4	6·69	65·6	11·85	89·4	12·93
90·9	6·95	77·1	11·73	115·6	12·59
118	8·30	87·7	11·74	128·6	12·49
130	9·44	99·3	11·89	141·5	12·48
143	11·43	111·8	12·23	153·4	12·50
155	13·58	127·2	13·00	176·3	12·64
167	15·80	145·4	15·19	198·3	12·97
189	20·72	157·2	17·28	229·0	13·90
				242·9	14·50
				257·7	15·29

Now strong acids, such as hydrochloric acid, when titrated at this high dilution with sodium and barium hydroxides, show the same correct turning points and strictly comparable curves. The differences again are entirely due to the differences in the mobilities of the sodium and barium ions, and accordingly the HCl–$Ba(OH)_2$ figures are not quoted. On the other hand, weak acids such as acetic, when titrated with these two alkalis, show quite different curves, and give no indication of the *true* end point. It is of interest, however, that at these high dilutions these curves show remarkably good agreement with the theoretical titration results deduced by Eastman (*loc. cit.*). With the platinum sols, whilst the curves of sodium and potassium hydroxides are comparable, and those of barium and calcium hydroxides are also comparable, Table III and Fig. 3 show that the sodium and barium hydroxide curves differ radically, the minima appearing at $44 \times 10^{-6}N$ and $68 \times 10^{-6}N$, respectively. It is therefore evident that platinum sols are not strictly comparable with strong acids. On the other hand, they seem to be far stronger acids than acetic; in fact, their behaviour indicates that they approximate more closely to strong than to weak acids. The author believes that they are really unique, and that they cannot strictly be compared either with strong or with weak acids. This belief is based, not only upon the above facts, but also upon certain peculiarities which were noticed in every platinum sol titration: all conductivity readings showed a steady drift if followed over some considerable time; the drift was very slow and if time were allowed for each to come to equilibrium, every titration would have spread itself over many days. (An attempt is now being made to follow the complete equilibrium titrations.) Some pre-

liminary investigations showed that these drifts were so slow that if the titrations were carried out fairly rapidly their effects could be neglected. Accordingly all titrations were performed within a total time limit of 80 minutes.

Discussion.

The explanation of the various phenomena outlined above appears to be as follows. The pure platinum sol contains a certain amount of relatively free or "diffused" hydrogen ions which contribute the greater part of the conductivity; further, each platinum anion has a surface layer (or double layer) of non-diffused hydrogen ions. Any temperature change causes a disturbance in the equilibrium between the diffused and the surface hydrogen ions, and all such rearrangements are not instantaneous but measurably slow. This explains the temperature lag invariably obtained with pure platinum sols (see p. 2602). Boiling not only disturbs the equilibrium, but as the conductivity never reverts to its previous value, it would appear that boiling breaks up the complex anion, or at least sets free from it further hydrogen ions, which were probably held in the interior.

On the addition of a small quantity of a base, *e.g.*, sodium hydroxide, we have a particularly favourable and simple colloid system to deal with, for the solution contains only sodium, hydrogen, and colloid complex ions, and no foreign anions at all. The added base immediately neutralises some of the free hydrogen ions, and as this disturbs the hydrogen-ion equilibrium, some of the surface ions diffuse into the solution. In other words, the platinum sol behaves as a weak acid, but with the difference that, whereas weak acid ionic equilibria are instantaneous, these are measurably slow. There is, however, a second and even more important difference. It is well known that coagulated colloids always carry down with them ions of the opposite charge (see, *e.g.*, Whitney and Ober, *J. Amer. Chem. Soc.*, 1901, **23**, 842; Gann, *Koll.-Chem. Beih.*, 1916, **8**, 127; Freundlich, *Z. physikal. Chem.*, 1910, **73**, 385).

It must be concluded, therefore, that in the case under discussion some of the sodium ions go to the surface, and that a definite sodium-ion equilibrium is reached. Platinum sols thus differ from weak acids in that their "salts" are not wholly ionised. The rate of this ionic rearrangement would probably differ for different kations, but in any case the results indicate that it is not instantaneous. If these equilibria were all infinitely slow, then the platinum sols would titrate as strong acids. The curves show that these rearrangements are actually taking place during the time limit of the experiment. All the readings before (and for a short distance after) the neutral point were drifting towards a greater conductivity, due to the greater mobility of the hydrogen ions leaving the surface com-

pared with the sodium ions joining the surface. Towards the latter part of the titration the drift was in the opposite direction owing to the latter effect predominating, the sodium-ion concentration in the solution being now abnormally high.

The difference in the titration end points obtained with univalent and with bivalent bases is due, not only to the difference in the various equilibrium ratios (or equilibrium constants) for the different kations, but also to the different rates at which these equilibria are set up. The fact that the univalent bases give the same acid (titration) values as those obtained on the assumption that the hydrogen ion contributes practically the whole of the conductivity of the pure sol, may be due to a similarity in the univalent equilibrium ratios and equilibrium rates. On the other hand, it is not beyond question that the true acid concentration is really less than that obtained by these methods. An attempt has been made to settle this matter by a determination of the p_H of the pure sol with the quinhydrone electrode. Steady values are obtained and these are always lower than those read off from the titration curves, but it has not yet been determined whether quinhydrone acts normally in the presence of colloidal platinum. Work in this direction is proceeding. Colorimetric tests are out of the question; and the hydrogen electrode itself gives varying and untrustworthy values in these unbuffered solutions.

The slow equilibria between diffused or free ions and ions at the surface seem to be of fundamental importance in the coagulation of colloids. For instance, it is well known that if the bare minimum of electrolyte necessary to produce coagulation is added to a colloidal solution, the coagulation is invariably slow and may extend over several hours and even days. This is evidently due to the slowness of the equilibria under discussion. Further, according to Gann (*Koll.-Chem. Beih.*, 1916, **8**, 65), Steiner (*Z. physikal. Chem.*, 1910, **73**, 507), and Galecki (*Z. anorg. Chem.*, 1912, **74**, 174), the rate of these slow coagulations is best expressed by an empirical autocatalytic equation. No satisfactory explanation has so far been advanced for this, but the following qualitative suggestion may ultimately be of value. Before coagulation can occur a certain quantity of the coagulating ion has to move to the surface. This rearrangement being slow, a definite time interval will elapse over which practically no coagulation occurs. As the colloid particles vary in size, in shape, and in total charge, then, as the necessary equilibria are approached, the particles which are more favourably constituted will reach their coagulation condition first, followed more and more rapidly by the other colloid particles, the tota effect thus appearing to be autocatalytic.

Summary.

Colloidal platinum prepared in water of specific conductivity 0·4 gemmho, and rigorously kept free from contamination, can be made to yield a specific conductivity of 41·2 gemmhos at 25°.

It is suggested that oxidation accompanies the sparking process and that a colloidal complex acid is formed.

Pure platinum sols have been titrated with various bases, and the titration curves are discussed. Whilst the platinum sols titrate more like strong acids than weak acids, they cannot strictly be compared with either.

There appears to be a slow equilibrium between the diffused hydrogen ions and the hydrogen ions held at the surface of the complex platinum anion.

A similar equilibrium exists for any other added kation.

The consequences of the slow velocities of these equilibria are discussed.

THE UNIVERSITY OF ADELAIDE,
SOUTH AUSTRALIA.

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CCCXLVI.—*The Configuration of the Ammonium Ion. Part II. Geometrically Isomeric Quaternary Ammonium Salts derived from 4-Phenyl- and 4-Hydroxy-piperidine.*

By WILLIAM HOBSON MILLS, JOHN DAVIES PARKIN, and WILLIAM JOSEPH VICTOR WARD.

WITH the view of obtaining experimental evidence with regard to the distribution of the valencies of the nitrogen atom * in the quater-

* With regard to the stereochemistry of tervalent nitrogen I would take this opportunity to point out that the optical activity of the pyridylhydrazone of *cyclo*hexylene dithiocarbonate, which Mills and Schindler (J., 1923, **123**, 312) regarded as evidence of the non-planar distribution of the valencies of the doubly linked tervalent nitrogen atom, is capable of a different interpretation. At the time that the work was carried out we were of opinion that the dithiocarbonate was necessarily derived from the *cis*-form of the dithioglycol and our conclusions were based on this assumption. In view, however, of the remarkable investigations of Hückel and his co-workers (*Annalen*, 1925, **441**, 1; 1926, **451**, 109, 132; 1927, **453**, 163), from which it appears that *trans*-forms of the dicyclic compounds decalin, β-hydrindanone, and decahydroquinoline are not only capable of existence, but may even be more stable than the corresponding *cis*-forms, this view can no longer be upheld and I am now of opinion that the optically active hydrazone is probably to be regarded as a derivative of the *trans*-dithioglycol, and if this is the case the pyridylhydrazone is molecularly dissymmetric however the valencies of the doubly-linked nitrogen atom are disposed.—W. H. M.

nary ammonium ion Mills and Warren (J., 1925, **127**, 2507) prepared and examined some of the salts of 4-phenyl-4′-carbethoxybispiperidinium-1 : 1′-spiran. They showed that these salts could be obtained in optically active forms and pointed out that the pyramidal configuration for the ammonium ion (which might perhaps be regarded as *a priori* the more probable on the older view that the electric charge on the ion was stereochemically equivalent to the directly linked acid radical in the non-ionised salt) was thereby excluded and gave reasons for concluding that the ion consequently had the *tetrahedral* configuration (as was more probable on the electronic theory of molecular structure).

In the present communication an account is given of another and independent method of investigating the same question. Since in the ammonium ion the nitrogen atom and the four attached radicals do not lie in the same plane, it was to be anticipated that geometrical isomerism should occur among the quaternary salts of the 4-substituted piperidine bases. Such isomerism we have found does, in fact, exist and its investigation provides a means of obtaining a decision between the pyramidal and the tetrahedral configuration of the ammonium ion. For if the ammonium ion has the pyramidal configuration, then, as will be evident from Fig. 1,* every 4-substituted quaternary piperidinium salt, $RCH<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NR'R''X$, should be capable of existence in two geometrically isomeric forms even although the two radicals R′ and R″ attached to the nitrogen atom might be identical. Each isomeride would be a racemic compound when these radicals were different, and a simple substance when they were identical, but in spite of this, if the isomerism could be detected in the one case it should also be demonstrable in the other. If, on the other hand, the ammonium ion has the tetrahedral configuration (Fig. 2) it is evident that geometrical isomerism could only occur when the radicals R′ and R″ were different and would disappear if they became identical.

We have examined salts of five quaternary bases derived from 4-substituted piperidines, three with different radicals R′ R″ (type I), and two with identical radicals R′R′ (type II) attached to the nitrogen atom.

* The rings in this and the following diagrams are represented plane for simplicity. There is an evident difficulty in representing piperidinium salts according to the Bischoff theory of the pyramidal configuration of ammonium salts, for it involves the replacement in *cyclo*hexane of a methylene group with a valency angle of 110° or more by an ammonium residue with a valency angle of less than 90°.

The difference between the two types proved to be clearly marked. The salts of type I, formed from a tertiary base,

$$RCH<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NR',$$

and an alkyl halide, R''X, all showed themselves, when subjected to fractional crystallisation, to be mixtures of pairs of isomerides. On the other hand, the salts of type II, prepared in a corresponding manner, proved to be homogeneous.

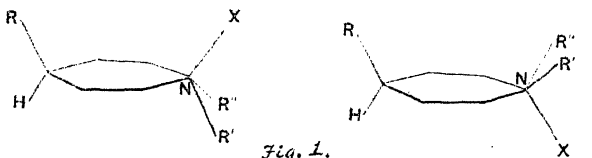


Fig. 1.

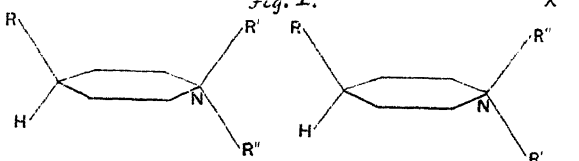


Fig. 2.

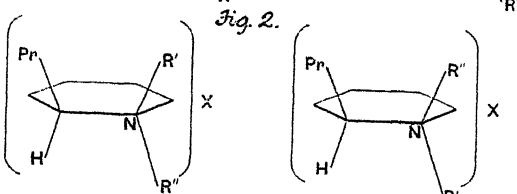
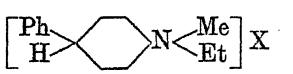
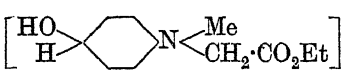
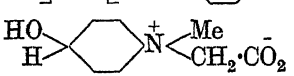


Fig. 3

The salts investigated were prepared from 4-phenylpiperidine and from 4-hydroxypiperidine. From the former compound were obtained the iodides and perchlorates of phenylmethylethylpiperidinium (I) and phenylbenzylethylpiperidinium and also phenyldiethylpiperidinium iodide and phenyldipropylpiperidinium iodide. From the latter compound the methobromides of 4-hydroxypiperidylacetic acid and of its ethyl ester (II) were prepared, as well as

(I.)  (II.) 

 (III.)

the corresponding betaine (III). Each of these salts in which two different radicals were attached to the nitrogen atom (salts of type I) was found to exist in two isomeric forms, as is shown in the following table :

Salts of type I.

Salt.	M. p. of *α*-isomeride.	M. p. of *β*-isomeride.
4-Phenyl-1-methyl-1-ethylpiperidinium iodide...	180°	140°
4-Phenyl-1-methyl-1-ethylpiperidinium perchlorate	135	159
4-Phenyl-1-benzyl-1-ethylpiperidinium iodide ...	240	210—215
4-Phenyl-1-benzyl-1-ethylpiperidinium perchlorate	208	189
Ethyl 4-hydroxy-1-piperidylacetate methobromide	221	206
Ethyl 4-hydroxy-1-piperidylacetate picrate	152—153	126
4-Hydroxy-1-piperidylacetic acid methobromide	170—172	210
4-Hydroxy-1-piperidylacetic acid methylbetaine	271—272	266—267

The salts of type II were found to consist of one form only. They had a sharp melting point and systematic fractional crystallisation gave no indication of the existence of a second modification.

Salts of type II.

	M. p.
4-Phenyl-1 : 1-diethylpiperidinium iodide	177°
4-Phenyl-1 : 1-dipropylpiperidinium iodide	190

In view of the evident possibility of the existence of geometrical isomerism in these salts and the absence, as far as can be seen, of any other cause to which the isomerism could be due, it appears safe to conclude that the isomerism exhibited by the salts of type I actually is a geometrical isomerism of the type sought for dependent on the non-planar distribution of the valencies of the ammonium nitrogen atom. This clear-cut difference between the salts of the two types therefore demonstrates that the quaternary ammonium ion has not a pyramidal configuration. It shows that the two radicals R′ and R″ attached to the nitrogen atom are unequally distant from the group R attached to the 4-carbon atom. The quaternary ammonium ion therefore cannot have the pyramidal configuration, and the valencies of the nitrogen atom in this ion must accordingly be tetrahedrally disposed.

The isomerism exhibited by the salts of type I thus corresponds closely with the *cis-trans* isomerism which occurs among the substitution derivatives of *cyclo*hexane, the relationship between the two forms of, for example, phenylmethylethylpiperidinium being represented by tridimensional formulæ such as those in Fig. 2 (R = Ph, R′ = Me, R″ = Et).

Although it was easy to show by fractional crystallisation that the salts of type I, as produced by the combination of tertiary base and alkyl halide, were not homogeneous, the isolation of both stereoisomerides in a state of purity from the mixtures of the two of which the crude salts consisted was not easily effected. Fractional

crystallisation brought about more or less readily the separation and isolation of the excess of the less soluble (α-) isomeride, but special methods were required to extract the pure β-isomeride from the mixture left in the mother-liquors.

The separation was most easily effected in the case of the phenylbenzylethylpiperidinium iodides. By allowing solutions of the mixed isomerides of appropriate concentration to crystallise under "aseptic" conditions, usually the α-form only separated, the β-form remaining in supersaturated solution. On then decanting the supersaturated solution and scratching, the pratically pure β-isomeride crystallised.

In the other cases the more soluble β-iodide could only be isolated through the replacement of the iodine by another acid radical which gave a less soluble salt with the β- than with the α-base. This β-salt could then be isolated in a state of purity and converted into pure β-iodide.

Thus in the case of α- and β-phenylmethylethylpiperidinium the solubilities of the perchlorates are in the inverse order of those of the iodides. The pure β-perchlorate could accordingly be isolated from the mixed perchlorates and gave on treatment with potassium iodide the pure β-iodide.

Similarly with the 4-hydroxypiperidinium salts; by fractional crystallisation of the mixed ethyl hydroxypiperidylacetate methobromides only the less soluble α-salt could be isolated. The more soluble of the two ester methobromides corresponds, however, with the less soluble of the two methylbetaines and the pure β-methylbetaine could therefore be obtained and from it the other salts of the β-series.

The stereoisomeric salts have considerable stability; no tendency to intertransformation was observed at the ordinary temperature. For example, when α-phenylmethylethylpiperidinium perchlorate was converted into iodide and then reconverted into perchlorate, pure α-perchlorate of melting point 159° was obtained. Transformation from one series to the other could, however, be brought about by heating. The change could be most easily observed with the phenylbenzylethylpiperidinium iodides. The more soluble β-iodide melts at 210—215°. If kept slightly above 215°, the molten salt resolidifies and the resolidified material is the α-isomeride, for it shows the melting point of that modification (240°, decomp.) and on conversion into perchlorate yields the pure α-perchlorate.

The relative quantities of the stereoisomeric salts produced in these additions of alkyl halides to 4-substituted tertiary piperidine bases were examined with the aid of melting point–composition curves in two of the cases investigated, namely, the addition of benzyl

chloride to phenylethylpiperidine and of ethyl bromoacetate to hydroxymethylpiperidine. In each case the quantities of the two isomerides formed were approximately in the ratio of 2 to 3. There is thus no great disproportion in the relative amounts of the two isomerides produced.

The isomerism of the quaternary ammonium salts here described is closely allied to the isomerism observed by Scholtz among the quaternary salts derived from coniine (*Ber.*, 1904, **37**, 3627; 1905, **38**, 595). Scholtz found that when an alkyl halide R'X combined with a 1-alkyl derivative of *d*-coniine, $CH_2<\begin{matrix}CH_2\text{-}CHPr\\CH_2\text{—}CH_2\end{matrix}>NR$, to form a quaternary salt the product was a mixture of two isomerides. Since the salts thus formed necessarily contained two asymmetric atoms, namely, the asymmetric carbon atom already present in the coniine and a newly formed asymmetric nitrogen atom, the isomerides were evidently the diastereoisomeric compounds (*d*C·*d*N), (*d*C·*l*N) and such isomerism should occur whatever the configuration of the quaternary ammonium nitrogen. The observations of Mills and Warren (*loc. cit.*) together with those described in the present communication show, however, that Scholtz's isomeric salts were *cis-trans* isomerides of the type indicated in Fig. 3.

Experimental.

A. Derivatives of Phenylpiperidine.

1-Alkyl Derivatives of 4-Phenylpiperidine.—4-Phenylpiperidine is shaken at the ordinary temperature with the alkyl iodide (1 mol.) and 10% aqueous sodium hydroxide (1·1 mols.). When the interaction is complete, the tertiary base (and unchanged phenylpiperidine) are extracted with ether. To remove the phenylpiperidine, the mixture is shaken with benzoyl chloride and alkali for 5—10 minutes at 50—60°. The tertiary base, and the benzoylphenylpiperidine thus formed, are taken up in ether and the former is extracted with dilute sulphuric acid from the ethereal solution. It is then isolated in the usual way, being finally purified through the crystallisation of an appropriate salt.

4-Phenyl-1-methylpiperidine was prepared from methyl iodide and phenylpiperidine by the above described method, but as the reaction is vigorous ether was used as a diluent. The base can also be prepared, as has been found by one of us and Mr. F. N. Kerr, by heating phenylpiperidine hydrochloride with formalin. It was purified by crystallisation of its perchlorate from ether–alcohol. The perchlorate forms felted needles, m. p. 106—107°, readily soluble in alcohol but sparingly in water and melting under water at about 25°. The pure *base* is a colourless liquid, m. p. 9°, b. p. 122—123°/

11 mm. (Found: C, 82·2; H, 9·8; N, 8·0. $C_{12}H_{17}N$ requires C, 82·2; H, 9·8; N, 8·0%). The *hydrochloride* (platelets from ether–alcohol) melts at 196—198° (Found: Cl, 16·6. $C_{12}H_{17}N,HCl$ requires Cl, 16·75%). The picrate melts at 244° (decomp.).

4-*Phenyl*-1-*ethylpiperidine*. The reaction between ethyl iodide, phenylpiperidine, and aqueous alkali proceeds slowly in the cold, 8—10 hours' shaking being required. The tertiary *base* was purified by crystallising the perchlorate (m. p. 112°) from alcohol. It is a liquid, m. p. 11°, b. p. 137°/11 mm. (Found: C, 82·3; H, 10·1; N, 7·7. $C_{13}H_{19}N$ requires C, 82·5; H, 10·1; N, 7·4%). The *hydrochloride* has m. p. 203—205° (Found: Cl, 15·6. $C_{13}H_{19}N,HCl$ requires Cl, 15·7%).

4-*Phenyl*-1-n-*propylpiperidine* was prepared by shaking *n*-propyl iodide, phenylpiperidine, and aqueous alkali together for 20 hours at room temperature, the final purification being effected through the perchlorate (m. p. 160—162·5°), which was recrystallised from ether–alcohol. The *base* is liquid at the ordinary temperature (m. p. 13°, b. p. 150°/11 mm.) (Found: C, 82·1; H, 10·5; N, 7·1. $C_{14}H_{21}N$ requires C, 82·7; H, 10·4; N, 6·9%). The *hydrochloride*, m. p. 250° (decomp.), is not very soluble in cold water (Found: Cl, 14·7. $C_{14}H_{21}N,HCl$ requires Cl, 14·8%).

α-4-*Phenyl*-1-*methyl*-1-*ethylpiperidinium Iodide*.—The α-modification of this salt is most easily isolated from the mixture formed by the combination of ethyl iodide with 4-phenyl-1-methylpiperidine, the combination being brought about by boiling the base with the alkyl iodide for 2 hours.

The product, after being dissolved in alcohol and precipitated with ether, melted at 152—154°. By fractional crystallisation from ether–alcohol of the mixture of the two iodides it could be resolved into a less soluble fraction, m. p. 170°, and a more soluble fraction, m. p. 148°. Since the iodides were only slowly separated by the fractionation, they were converted into perchlorates by dissolving them in water (10 g. in 500 c.c.) at 40—50° and adding an exactly equivalent quantity of silver perchlorate in aqueous solution, a little perchloric acid being also added to promote the coagulation of the silver iodide.

The less soluble iodide fraction gave a perchlorate which, recrystallised from alcohol, yielded the pure α-perchlorate in felted needles of constant melting point 135°. On conversion of this perchlorate into iodide by dissolving it in a concentrated aqueous solution of potassium iodide, extracting the salt with chloroform, and precipitating it from the dried chloroform solution with ether, the pure α-*iodide* was obtained as colourless plates, m. p. 180—181° (Found: C, 50·7; H, 6·8; I, 38·0. $C_{14}H_{22}NI$ requires C, 50·75; H, 6·7; I, 38·3%).

It melts under water, in which it is not very soluble, dissolves readily in alcohol, and is exceedingly soluble in chloroform.

β-4-*Phenyl*-1-*methyl*-1-*ethylpiperidinium iodide*. This modification is most easily isolated from the mixture of the two forms of the quaternary iodide which is produced by the addition of methyl iodide to phenylethylpiperidine. After completion of the combination, which proceeded with evolution of heat, the resulting crystalline cake was dissolved in a little alcohol and reprecipitated by the addition of 2—3 volumes of ether. The mixture of iodides thus obtained, m. p. 146—147·5°, was converted into perchlorate by treating it with silver perchlorate as described above. The salt which crystallised directly from the aqueous solution consisted almost entirely of the β-form and readily gave the pure β-perchlorate on crystallisation from alcohol. The β-perchlorate crystallises in plates, m. p. 159°, and is sparingly soluble in cold alcohol and very sparingly in cold water. On conversion into iodide the pure β-*iodide* was obtained. This salt crystallises in plates which liquefy in contact with cold water. It is dimorphous, the two forms melting at 140° and 146°. It always crystallises from solution in the form melting at 140°, but usually resolidifies in the form melting at 146° (Found: C, 50·75; H, 6·55; I, 38·3. $C_{14}H_{22}NI$ requires C, 50·75; H, 6·7; I, 38·3%).

The aqueous solution from which the β-perchlorate had crystallised was evaporated almost to dryness at 30—40° under diminished pressure. By fractional crystallisation from alcohol of the salt thus obtained, a further small quantity of pure β-perchlorate could be separated, but the bulk consisted of a mixture melting at 115° and crystallising unchanged from alcohol or water. This mixture, on conversion into iodide, gave a product, melting at 150°, from which, by crystallisation from ether–alcohol, an iodide of m. p. 170° was obtained and this on conversion into perchlorate gave the pure α-perchlorate identical in melting point and mixed melting point (135°) with the α-perchlorate obtained as described in the preceding section.

α- *and* β-4-*Phenyl*-1-*benzyl*-1-*ethylpiperidinium iodides*. Equivalent quantities of 4-phenyl-1-ethylpiperidine and benzyl chloride were heated at 100° for 2—3 hours. The product was dissolved in water, small quantities of unchanged material were removed by extraction with ether, and the mixed quaternary perchlorates, which are almost insoluble in water, were precipitated by adding a concentrated solution of sodium perchlorate.

From the mixture, m. p. 182°, the very sparingly soluble α-salt was obtained by extraction with alcohol. The mixed salt (20 g.) was boiled with alcohol (200 c.c.), and the solution filtered hot.

The mixture of maximum solubility, m. p. 172°, was deposited on cooling and the mother-liquor was used again to extract the undissolved salt; the process was repeated until the crystals deposited showed a melting point distinctly above 172°. The residue, which melted above 200°, was then nearly pure α-perchlorate and was recrystallised from a large volume of alcohol until it melted constantly at 208°, the melting point of the pure salt.

The β-perchlorate was obtained from the mixture of maximum solubility by a method based on its tendency to form supersaturated solutions. Alcohol was stirred with the mixture at 35—40° until practically saturated. The resulting solution was "sterilised" by heating to the boiling point and after being seeded with a few crystals of the carefully purified α-form was allowed to remain overnight, the neck of the flask being plugged with cotton wool. The α-modification then usually crystallised alone in slender needles and the decanted solution deposited the β-modification on scratching. Recrystallised from alcohol, it melted at 189°.

Mixtures of the two perchlorates have the following melting points:

% β-Form	0	20	35	50	63	75	85	100
M. p.	208°	195°	184°	172°	170°	176°	182°	189°

To convert the perchlorates into iodides, the salt (2 g.) was boiled with absolute alcohol (200 c.c.) and finely powdered potassium iodide (10 g.), and the solution filtered after 1 hour. The iodide deposited on cooling the filtrate and adding an equal volume of ether was recrystallised from aqueous alcohol containing 30—40% of water. In this manner from the α- and β-perchlorates the pure α- and β-iodides were obtained.

α-4-*Phenyl*-1-*benzyl*-1-*ethylpiperidinium iodide* crystallises in iridescent plates, m. p. 240° (decomp.) (Found: C, 58·9; H, 6·6; I, 31·2. $C_{20}H_{26}NI$ requires C, 58·9; H, 6·4; I, 31·2%), and β-4-*phenyl*-1-*benzyl*-1-*ethylpiperidinium iodide* in needles, m. p. 210—215° (Found: C, 58·8; H, 6·6; I, 31·2%).

The molten β-iodide resolidifies when kept above its melting point and melts again at 240°, the melting point of the α-iodide. It was shown that the resolidified material was in fact the α-iodide by dissolving it in water and precipitating the pure α-perchlorate with sodium perchlorate.

4-*Phenyl*-1 : 1-*diethylpiperidinium iodide*. Phenylethylpiperidine was boiled with an excess of ethyl iodide for 2 hours. The resulting crystalline cake was fractionally crystallised from alcohol and ether–alcohol, but no separation could be detected, all the fractions melting at 177°, with the exception of the last, which melted at 176°, evidently on account of the presence of a trace of accidental impurity (Found:

C, 52·2; H, 7·0; I, 36·9. $C_{15}H_{24}NI$ requires C, 52·2; H, 7·0; I, 36·9%)

4-*Phenyl*-1 : 1-*di*-n-*propylpiperidinium iodide*. Phenyl-*n*-propylpiperidine was boiled under reflux for several hours with excess of *n*-propyl iodide. The resulting quaternary salt, fractionally crystallised from alcohol and alcohol–ether, showed no sign of resolution into isomeric modifications but melted constantly at 190° (Found: C, 54·7; H, 7·4; I, 34·2. $C_{17}H_{28}NI$ requires C, 54·7; H, 7·5; I, 34·0%).

We are indebted to Mr. D. Webb, of Emmanuel College, for assistance with the preparation and analysis of this and the foregoing compound.

B. Derivatives of Hydroxymethylpiperidine.

4-*Hydroxy*-1-*methylpiperidine*.—1-Methyl-4-pyridone (22·5 g.) (Lieben and Haitinger, *Monatsh.*, 1885, **6**, 300) was dissolved in boiling absolute alcohol (225 c.c.), and sliced sodium (75 g.) added as rapidly as possible. When the action had abated, absolute alcohol (750 c.c.) was added in portions of 50 c.c. After the sodium had dissolved, water was added and the mixture was distilled with steam until 1 litre of distillate had been collected. The product was then driven over with superheated steam. The aqueous distillate (2 l.), acidified with hydrochloric acid and evaporated, left a brownish residue which, crystallised from absolute alcohol, gave 4-*hydroxy*-1-*methylpiperidine hydrochloride* (20 g.) as colourless prisms, m. p. 157—158°; these were hygroscopic, very soluble in water, easily soluble in hot, and sparingly soluble in cold alcohol (Found: Cl, 23·5. $C_6H_{13}ON,HCl$ requires Cl, 23·4%). By decomposing this hydrochloride with alkali the free base (Emmert, D.R.-P. 292871) was obtained as an oil, b. p. 105°/18 mm., which we found to crystallise on keeping (m. p. 28°). The *hydrobromide* formed colourless needles, m. p. 139—140°, from alcohol (Found: Br, 40·9. $C_6H_{13}ON,HBr$ requires Br, 40·8%).

Ethyl α-4-*Hydroxy*-1-*piperidylacetate Methobromide*.—4-Hydroxy-1-methylpiperidine (12·2 g.) and ethyl bromoacetate (23·7 g.) dissolved in benzene (180 g.) reacted at room temperature with the formation of quaternary bromide, the mixture setting to a crystalline mass which was collected after 20—24 hours. The product was a mixture of the α- and β-bromides, m. p. about 204°, and the yield was practically quantitative (Found: Br, 28·2. $C_{10}H_{20}O_3NBr$ requires Br, 28·3%).

The α-modification of the salt was obtained by boiling out the product from the above quantities with absolute alcohol (90 c.c.), filtering the hot solution, and boiling the residue successively with

50 c.c. and 40 c.c. of alcohol. The residue left (6·9 g., m. p. 220°), crystallised from rectified spirit, had m. p. 221° (decomp.), which could not be raised by further treatment.

Ethyl α-4-hydroxy-1-piperidylacetate methobromide forms colourless prisms very soluble in water and sparingly soluble in alcohol (Found: C, 42·7; H, 7·1; Br, 28·3. $C_{10}H_{20}O_3NBr$ requires C, 42·6; H, 7·1; Br, 28·3%). The *picrate* forms yellow needles, m. p. 152—153°, moderately easily soluble in alcohol or water (Found: N, 13·1. $C_{16}H_{22}O_{10}N_4$ requires N, 13·0%).

α-Methylbetaine of 4-Hydroxypiperidylacetic Acid.—An aqueous suspension of freshly prepared silver oxide was gradually added to ethyl α-4-hydroxypiperidylacetate methobromide until the brown colour of the oxide persisted. The filtrate from the silver bromide was evaporated, finally over sulphuric acid in a vacuum, and the residue was dissolved in hot alcohol, a little brown insoluble matter being removed by filtration. On cooling, the betaine was deposited as pearly leaflets, m. p. 271—272°, moderately easily soluble in alcohol and easily soluble in water (Found: C, 55·2; H, 8·4. $C_8H_{15}O_3N$ requires C, 55·4; H, 8·7%).

α-4-Hydroxypiperidylacetic Acid Methobromide.—The above described betaine was converted into the corresponding methobromide by dissolving it in a slight excess of hydrobromic acid and evaporating the solution on the water-bath under diminished pressure. The residue, crystallised from alcohol, gave the *methobromide* as colourless prisms, m. p. 170—172° (Found: Br, 31·2. $C_8H_{16}O_3NBr$ requires Br, 31·5%).

If the betaine is dissolved in less hydrobromic acid, a *basic salt* is obtained containing two molecules of betaine to one molecule of hydrogen bromide. It crystallised from alcohol in clusters of fine, radiating needles, m. p. 215—218° (decomp.) (Found: Br, 18·9. $C_{16}H_{31}O_6N_2Br$ requires Br, 18·7%). Similar compounds were obtained by Krüger from pyridine betaine (*J. pr. Chem.*, 1891, **43**, 289). The substance probably has the constitution

$$\bar{Br}\left[C_5H_9(OH)\overset{+}{N}<\begin{matrix}Me & Me\\ CH_2\cdot CO_2 & \end{matrix}>\overset{+}{N}C_5H_9\cdot OH\right]\begin{matrix}\\ \\ CH_2\cdot CO_2H\end{matrix}$$

the dotted line representing an electro-valency.

β-Methylbetaine of 4-Hydroxypiperidylacetic Acid.—The filtrate from the first extraction with alcohol of crude ethyl hydroxypiperidylacetate methobromide (p. 2622) was evaporated and the residue (11·5 g.) was converted into betaine with silver oxide. The resulting mixture of the two betaines was extracted with cold alcohol (15 c.c.), which removed most of the more soluble α-compound; the residue, crystallised from rectified spirit, gave the pure *β-methyl-*

betaine as small, beautifully formed prisms, m. p. 266—267° (decomp.), sparingly soluble in alcohol, easily soluble in water. The crystals contain one molecule of water of crystallisation which is lost at 100° (Found : C, 50·2; H, 9·1; H_2O, 9·4. $C_8H_{15}O_3N,H_2O$ requires C, 50·2; H, 9·0; H_2O, 9·4%. Found for the anhydrous compound : C, 55·6; H, 8·7. $C_8H_{15}O_3N$ requires C, 55·4; H, 8·7%). The hydrated and the anhydrous substance showed the same melting point : a mixture with the α-betaine melted at 249—251°.

β-4-*Hydroxypiperidylacetic acid methobromide* was prepared by treating the corresponding betaine with hydrobromic acid in the manner described for the α-modification; it crystallised from alcohol in prisms, m. p. 210° (decomp.) (Found : Br, 31·5. $C_8H_{16}O_3NBr$ requires Br, 31·5%). A *basic salt* corresponding with that formed from the α-betaine could be isolated by using less hydrobromic acid. It formed colourless needles, m. p. 220—221° (decomp.), from alcohol (Found : C, 44·7; H, 7·2; Br, 18·9. $C_{16}H_{31}O_6N_2Br$ requires C, 44·9; H, 7·3; Br, 18·7%).

Ethyl β-4-*Hydroxypiperidylacetate Methochloride.*—The β-betaine (1 g.) was covered with absolute alcohol (10 c.c.) and dry hydrogen chloride was passed in, with cooling, to saturation; the betaine then gradually dissolved. After standing a day, the mixture was evaporated in a vacuum over sulphuric acid and solid sodium hydroxide; the residue, recrystallised from alcohol, gave the pure *ester methochloride* (0·93 g.) as rosettes of leaflets, m. p. 206° (decomp.) (Found : Cl, 14·9. $C_{10}H_{10}O_3NCl$ requires Cl, 14·9%).

The corresponding *picrate* was prepared from the chloride by double decomposition with sodium picrate; it formed golden-yellow needles, m. p. 126°, from water (Found : N, 13·0. $C_{16}H_{22}O_{10}N_4$ requires N, 13·0%). The pure β-picrate could not be obtained from the mixed picrates formed by the action of sodium picrate on the more soluble fractions of the original ester methobromide. Crystallisation from several different solvents gave only a mixture of unchanged m. p. 118—120·5°.

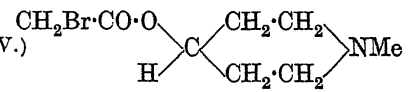
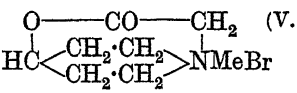
Ethyl β-4-*Hydroxypiperidylacetate Methobromide.*—The β-betaine (2 g.) and 9% alcoholic hydrogen bromide (30 c.c.) were allowed to stand over-night and then refluxed gently for 8 hours. The solid slowly dissolved on heating and, on cooling, the *ester methobromide* (2·2 g.; m. p. 205°) was deposited. After crystallisation from alcohol, in which it was moderately easily soluble, the pure compound of m. p. 206° was obtained (Found : C, 42·6; H, 7·2; Br, 28·1. $C_{10}H_{20}O_3NBr$ requires C, 42·6; H, 7·1; Br, 28·3%).

A series of mixtures of the α- and β-ester methobromides was prepared and the following melting points were observed :

% α-Salt.	M. p.	% α-Salt.	M. p.
0·0	206°	51·8	205°
13·1	205	69·7	208
26·1	203·8	81·0	211
33·4	203·5	89·0	214·3
41·9	203·8	100	221

A curve plotted from these data indicates that the two salts form a continuous series of solid solutions. The analytically pure mixture of the α- and β-bromides formed by the addition of ethyl bromoacetate to hydroxymethylpiperidine melted at 204°. This indicates that it contained either 22% or 42% of the α-salt, but the amount of α-salt isolated decides for the latter figure.

4-*Bromoacetoxy*-1-*methylpiperidine* (IV). It seemed not impossible that it might prove practicable to determine the configurations of the α- and β-series by relating compounds belonging to the one or the other to the lactone (V).

(IV.)  (V.) 

As neither the α- nor the β-methobromide of hydroxypiperidylacetic acid showed any tendency to lactonise on heating, 4-bromoacetoxy-1-methylpiperidine was prepared as a possible source of the lactone. A solution of 4-hydroxy-1-methylpiperidine (5·1 g.) in benzene (100 c.c.) was dropped with mechanical stirring during ¼ hour into bromoacetyl bromide (9 g.), and the mixture kept overnight. The benzene was decanted from the product, the hydrobromide of the required base, which had been deposited as a gum on the sides of the flask; this gum crystallised from alcohol in clusters of minute, radiating needles, m. p. 172°, very soluble in water and sparingly soluble in alcohol [Found: C, 30·3; H, 4·9; Br (ionic), 25·2. $C_8H_{15}O_2NBr_2$ requires C, 30·3; H, 4·8; Br (ionic), 25·2%]. We were unable to prepare the required lactone from the free base corresponding with this hydrobromide. Heated in benzene solution, it gave an amorphous solid, containing 2% too little bromine for the lactone, which was probably an impure polymeride. Heated in alcohol, it gave a mixture of the α- and β-methobromides of ethyl hydroxypiperidylacetate, indicating that alcoholysis of the bromoacetyl group had occurred followed by recombination of the products, hydroxymethylpiperidine and ethyl bromoacetate. That this lactone could not be prepared is not surprising, as its formation would involve the production of a tricyclic compound containing two 7-membered rings.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for grants which enabled two of

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UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, August 25th,* 1927.]

CCCXLVII.—*The Electrolysis of Potassium Chloride Solutions by Alternating Currents.*

By ARTHUR JOHN ALLMAND and HERBERT CHARLES COCKS.

THIS subject has been studied by Coppadoro (*Gazzetta*, 1905, **35**, ii, 604), using 42-cycle current and 3*N*-potassium or sodium chloride. With polished platinum electrodes and at room temperature, no electrolysis was noticed until a *C.D.* of 0·5 amp./cm.^{2} had been exceeded; above this threshold value, hydrogen was evolved and hypochlorite formed, oxygen also being detected after the electrolysis had been proceeding for some time. The electrodes were corroded, and to some extent went into solution as platinum compounds and as colloidal platinum; if the *C.D.* were not sufficiently high, they became platinised and electrolysis ceased. With graphite electrodes, no hypochlorite was formed below a *C.D.* of 10 amps./cm.^{2}, under which conditions the electrodes were considerably attacked. The hypochlorite current efficiencies were low, *e.g.*, 2% during a 30-minute run at 1 amp./cm.^{2}. After a time, a stationary hypochlorite concentration was reached, and further electrolysis produced chlorate. In a second paper (*ibid.*, 1906, **36**, ii, 321), Coppadoro reports experiments carried out at 50—70°, under which conditions chlorate, and not hypochlorite, is formed.

The work now recorded is a systematic study of the different factors which can affect this electrolysis when carried out at room temperature. In particular, the effects of frequency, current density, and concentration have been investigated. It may be said at once that, in so far as the conditions under which we have worked coincide with those of Coppadoro, our results are in agreement with his.

EXPERIMENTAL.

Apparatus.—The cell used in the great majority of the experiments consisted of a beaker of about 200 c.c. capacity, provided with a wooden lid. This carried (*a*) the capillary exit-tube of a glass hood of bell-jar shape, which dipped below the surface of the electrolyte to within 1—2 cm. of the bottom of the beaker, (*b*) a thermometer, and (*c*) the glass tubes into which the electrodes were sealed. These

tubes were bent back twice through 90°, so as to project upwards below the edge of and into the hood. The electrodes, spaced vertically and parallel to one another about 2 cm. apart, were 1 cm. square, and were carefully polished and burnished before each experiment. The cell itself stood in a large vessel of water, in order to keep down the temperature during electrolysis. The capillary exit led to the three-way tap of a gas-burette, which could also be connected with a Hempel gas-pipette containing alkaline pyrogallol. About 90 c.c. of electrolyte were placed in the cell and, by manipulation of the burette, made to fill completely the hood, the capillary connecting tube, and one bore of the three-way tap. The gas-burette, the other tap-bore, and the second connecting tube were then filled with water, and the whole was attached to the pyrogallol pipette. After electrolysis for a definite period of time, the evolved gases were passed over to the burette (care being taken to transfer all bubbles adhering to the sides of the hood), measured, and the oxygen content was determined. No attempt was made to estimate or to allow for any gases dissolved either in the electrolyte or in the burette liquid. No chlorine was detected at any time, and consequently, after subtracting the oxygen present, the residue was regarded as hydrogen. Immediately after the transfer of the gases, the cell liquid was made up to a definite volume, and analysed by the usual methods for hypochlorite and for total available oxygen. The presence of platinum in the solution caused the iodine–starch end-point to be rather less definite than usual, but did not appreciably affect the accuracy of the analysis.

The current used was hand-regulated by a variable resistance, and measured by a calibrated hot-wire ammeter. It was produced by one of two machines (a G.E.C. 16-pole alternator, capable of being run between the limits of 5 and 240 cycles, and a 24-pole alternator of inductor type, made by the Crocker–Wheeler Company, and giving 350—500 cycles) which have been described elsewhere (*Trans. Faraday Soc.*, 1925, **21**, 1).

Preliminary Experiments.—When graphite electrodes, 3*N*-potassium chloride, and a *C.D.* of 1 amp./cm.^{2} were used, electrolysis was inappreciable with 18 cycles, and only very slight at a frequency of 6 cycles. (With this very low frequency, we made no attempt to use higher *C.D.*'s. This could only have been done by reducing the size of the electrodes, the output of our machine under these conditions being small.) With polished platinum electrodes and a frequency $n = 6$, there was considerable electrolysis even at 0·3 amp./cm.^{2}. If the electrodes were platinised, the results were as with graphite. These experiments also showed the importance of determining the hypochlorite immediately after conclusion of the

electrolysis. In presence of the 3*N*-potassium chloride, decomposition was fairly rapid, even in the absence of platinum and platinum compounds.

Effect of Frequency and Current Density.—The experiments described in this section were all carried out with 3*N*-potassium chloride. The frequencies employed were $n = 5$—6, 21—22, 41, 50, 64, and 120 cycles per second. Depending on n (and therefore on the available output of the machine), the currents used varied between the limits of 0·1 and 2·5 amps. Low *C.D.*'s and high frequencies favoured platinisation of the electrodes. With $n = 6$, this was hardly perceptible, even with the lowest *C.D.*'s employed (0·1—0·3 amp./cm.^{2}); with $n = 22$, platinisation was appreciable with low *C.D.*'s, but very slight with 2—2·5 amps./cm.^{2}; with the higher frequencies, it was always very noticeable. In addition, a yellow deposit (probably potassium chloroplatinate) was sometimes found on the electrode; it was produced neither at the lowest nor at the highest *C.D.*'s, but usually at about 0·3—1 amp./cm.^{2}. It was less noticeable with high frequencies. Finally, with all except the lowest *C.D.*'s, the electrolyte became yellow or brownish-yellow and finally cloudy, and the more so as the electrolysis proceeded. On the assumption that the lessened tendency to formation of deposits of any kind on the electrodes at high *C.D.*'s is due to their being scoured by the rush of evolved gas, the facts mentioned are qualitatively consistent with the conception that ionisation of the normally passive platinum, like the other electrolytic processes (as will be seen), takes place the more readily during the anodic pulse the lower the frequency and the higher the *C.D.*; and that the reverse change takes place to a greater extent during the cathodic pulse the higher the frequency.

Only in one case ($n = 41$, $i = 2$ amps.) was any chlorate production noticed, and here there was definite local heating.

Table I contains a typical set of results. The current efficiencies are calculated, as throughout the paper, on a basis of actual coulombs passed, *i.e.*, assuming the current to have a sine wave form, the average current used for the calculation is 0·9 of the value in column 2, or $i_{\text{average}} = 2\sqrt{2}/\pi \,.\, i_{\text{effective}} = 0{\cdot}9\ i_{\text{effective}}$.

Fig. 1 shows the effect of *C.D.* on current efficiency for $n = 5$—6, 21—22, and 64. A remarkable feature in the curves for the lower frequencies is the abrupt changes in direction that occur at 0·3—0·4 and at about 1 amp., respectively. Fig. 2 exhibits the effect of frequency for currents of 1, 1·5, and 2 amps.

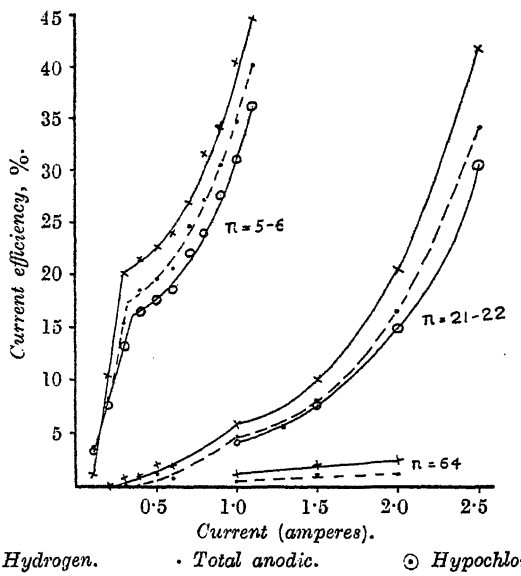
As Fig. 1 shows the current efficiency (for the lower frequencies) to be increasing very rapidly with the *C.D.*, a few experiments were carried out with very high *C.D.*'s and platinum wire electrodes. In

TABLE I.

Polished platinum electrodes, 1 cm.^{2}. Electrolyte, 3N-KCl. Frequency, 5—6 cycles. Temperature, 10—20°.

Time (mins.).	Current (r.m.s.) (amps.).	Current efficiencies, %. Hydrogen.	Hypochlorite.	Oxygen.	Total anodic.
120	0·1	1·1	3·3	0·22	3·5
60	0·2	10·7	7·8	0·56	8·3
40	0·3	20·3	13·3	2·3	15·6
30	0·4	21·6	16·7	2·1	18·8
24	0·5	22·9	17·8	2·1	19·9
20	0·6	24·2	18·7	2·1	20·8
17	0·7	27·1	22·3	2·7	25·0
15	0·8	31·8	24·2	3·2	27·4
10	0·9	34·4	27·8	2·9	30·7
10	1·0	40·6	31·3	3·6	34·9
6	1·1	44·9	36·4	3·9	40·3

FIG. 1.



× *Hydrogen.* · *Total anodic.* ⊙ *Hypochlorite.*

this case, the gases were not collected, and the cell used, of 35 c.c. capacity, was cooled externally by running water. Each electrode consisted of 8 mm. of platinum wire of 0·38 mm. diameter, and had therefore a total area of 0·09—0·1 cm.^{2}. They were spaced about 1·3 cm. apart. The results (Table II) show that the curves for these frequencies in Fig. 1 must soon bend over with increasing current and, from being convex, become concave.

C.D.'s exceeding 15 amps./cm.^{2} at 22 cycles caused the formation of sparks and arcs around the electrodes, which remained quite clean

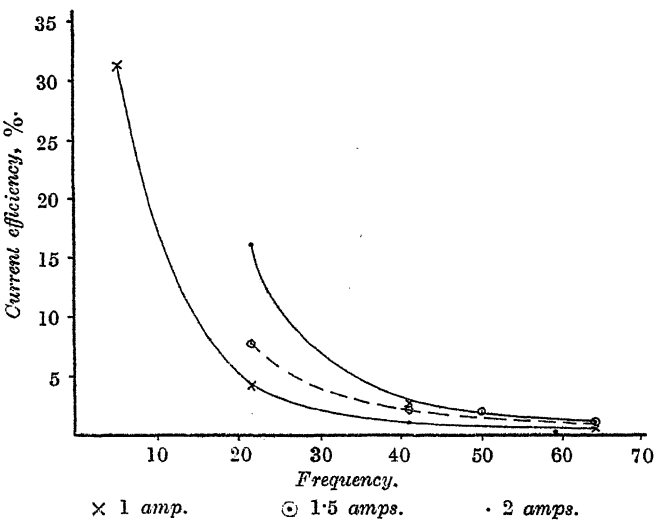
TABLE II.

Platinum wire electrodes, 0·1 cm.². Electrolyte, 3*N*-KCl.

Frequency.	Time (mins.).	Current (r.m.s.) (amp.).	Hypochlorite current efficiency, %.
5	15	0·4	65·6
6	30	0·3	64·4
22	5	1·0	61·1

in every case. At 5—6 cycles, the electrolyte also remained clear at these high *C.D.*'s, but became pale yellow in colour, whilst, with 22 cycles, it became dark brown or black. In all cases, good thiosulphate end-points were obtained (sharp change from blue to colourless).

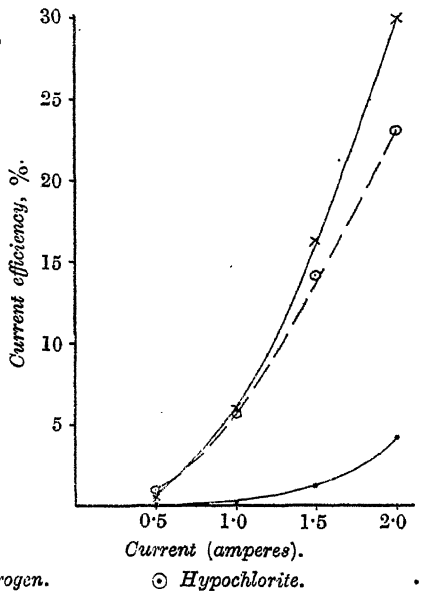
FIG. 2.



Whatever the *C.D.*, the total anodic current efficiency (hypochlorite plus oxygen) was less than the cathodic current efficiency (as in Table I, for $n = 6$). A determination of the quantity of platinum dissolved after one of the experiments indicated that about one-third of the usual deficiency could be accounted for in this way, assuming that the metal had dissolved in the quadrivalent state. In addition, the electrodes, carefully washed after electrolysis and then immersed in a colourless solution of acidified potassium iodide and starch, soon caused a slight colour to develop, showing that they contained traces of some oxidation product of platinum, the amount, however, being negligible in comparison with the "missing" oxygen. Formation of perchlorate was not tested for, but is very unlikely. As the products formed at the two electrodes were

collected together, the cause could not be a slight rectification. With platinum electrodes of unequal size in sulphuric acid, this does take place to a certain extent (Mengarini, *Electrician*, 1891, **27**, 334; Gundry, *Phil. Mag.*, 1906, **11**, 329; Vaillant, *Compt. rend.*, 1919, **168**, 687), and it was also observed by Ayrton and Perry (*Electrician*, 1888, **21**, 299) when using an ordinary Hoffmann voltameter. In our work, it seemed negligible, judging from the results of experiments carried out with a variety of *C.D.*'s and frequencies, a hot-wire ammeter and a moving-coil ammeter being in series in the circuit.

FIG. 3.



In some cases, indeed, we certainly noticed more gas coming off at one of the two apparently quite similar electrodes, but this does not necessarily indicate rectification.

Expressed in terms of oxygen gas, the maximum deficiency was of the order of 1 c.c. One possibility is that the missing gas had dissolved in the electrolyte or in the water in the measuring burette. Perhaps it was formed by spontaneous decomposition of the hypochlorite, and remained in a state of supersaturation, as is the case in the photodecomposition of chlorine water or of hypochlorous acid solutions (J., 1925, **127**, 822). It may be remarked that the alternating-current electrolysis of sulphuric acid between platinum electrodes has, on several occasions, been noticed to give a deficiency

of oxygen (Manœuvrier and Chappuis, *Compt. rend.*, 1888, **106**, 1719; Marsh, *Proc. Roy. Soc.*, 1920, **97**, 124).

Effect of Concentration.—A series of experiments was carried out on N-potassium chloride solutions, with frequencies varying between 6 and 180, and currents up to 2 amps. The electrodes became platinised in every case, but there was no formation of yellow deposit. The electrolyte became increasingly turbid (yellow or brown) as the electrolysis proceeded. Fig. 3 contains graphs of the data for $n = 21$, whilst in Table III are the results for $n = 5$—6 and $n = 21$—22, compared with the corresponding figures given by $3N$-potassium chloride.

TABLE III.

Frequency.	Current (r.m.s.) (amps.).	Cathodic current efficiency, %,		Hypochlorite current efficiency, %,	
		$3N$-KCl.	N-KCl.	$3N$-KCl.	N-KCl.
6	0·1	1·1	0·33	3·3	0·22
6	0·2	10·7	0·78	7·8	2·3
6	0·3	20·3	6·1	13·3	6·4
21	0·5	2·1	0·56	1·2	1·0
21	1·0	6·0	6·0	4·2	5·6
21	1·5	10·3	16·2	7·8	14·1
21	2·0	20·8	29·8	15·2	23·0

It will be noted that the curves for N-potassium chloride do not show the breaks which are such a marked feature in those for the $3N$-solution. Like the latter, their slope must clearly become less at higher *C.D.*'s. Corresponding to their continuous nature, the current efficiencies are seen to be lower at lower, and higher at higher, current densities than is the case with $3N$-potassium chloride. The effect of frequency is similar to that shown in Fig. 2.

A few experiments only were done with $0{\cdot}1N$-potassium chloride solutions, owing to the low conductivity and consequent tendency to temperature rise, with formation of chlorate. The results were of no particular interest.

Effect of Addition of Alkali.—These experiments, carried out with solutions of composition $3N$-KCl + $0{\cdot}1N$-NaOH, were suggested by the well-known fact that hypochlorites are more stable in alkaline than in neutral or acid solution. The results, compared with those given by a neutral solution, are shown in Table IV.

It will be seen that, whilst the yield of hypochlorite is lowered, that of both hydrogen and oxygen is increased by the addition of alkali, whilst the deficiency in the total anodic yield still persists. This last result appears to dispose of the suggested possibility of the deficiency being due to supersaturated oxygen resulting from chemical decomposition of the hypochlorite, for this was found to be very low in the alkaline solution.

TABLE IV.

Polished platinum electrodes, 1 cm.^{2}. Frequency, 6.
Temperature, 10—20°.

Current (r.m.s.) (amp.).	Current efficiencies, %. Neutral solutions. Hydrogen.	Hypochlorite.	Oxygen.	Total anodic.	Alkaline solutions. Hydrogen.	Hypochlorite.	Oxygen.	Total anodic.
0·5	22·9	17·8	2·1	19·9	27·1	17·0	8·0	25·0
0·8	31·8	24·2	3·2	27·4	34·4	22·0	8·3	30·3

Effect of Addition of Potassium Chromate.—It is well known that, in direct-current electrolysis of alkali-metal chlorides, the hypochlorite yield can be markedly increased by the addition of a chromate, its effect being to reduce considerably the cathodic reduction of hypochlorite ions which otherwise takes place, owing to the formation on the electrode of a film (" cathode diaphragm ") which is usually supposed to be chromium chromate. Experiments were consequently done with 3*N*-potassium chloride solutions containing, in addition, 1 g. of potassium chromate per litre. It is unnecessary to give the results in detail, as the effects were small. Quite definitely, however, there appeared to be a decrease in current efficiency at low, and an increase at high, current densities. This was observed with both 6- and 22-cycle current. The platinum also appeared to be less attacked. No platinum-black was formed, nor did the electrolyte become as cloudy as under similar conditions in the absence of chromate.

Effect of Stirring.—Experiments were carried out in the simple type of cell used for investigating the effect of high *C.D.*, a mechanically driven stirrer running at a fairly high speed being used. No attempt was made to collect the gases. The anticipated increase in current efficiency is seen to be marked (Table V).

TABLE V.

Frequency.	Current (r.m.s.) (amps.).	Hypochlorite current efficiency, %. Without stirring.	With stirring.
6	0·2	7·8	14·8
6	0·5	17·8	25·0
6	0·8	24·2	36·0
6	1·0	31·4	38·7
42	1·0	2·4	6·2
42	1·5	2·1	8·3

Limiting Hypochlorite Concentration.—These experiments were carried out in the same simple cell. Stirring was not employed, but the cell was kept cool by a stream of water running over it. With 25 c.c. of neutral 3*N*-potassium chloride and a current of 1·2 amps.

at a frequency of 6, the hypochlorite concentration rose, first rapidly, then slowly, to about 0·27—0·28*N* after a run of 2½—3 hours. Further electrolysis led to no further increase—on the contrary, a slight decrease was observed after 5 hours, the concentration falling to 0·26*N*. Considerable amounts of a brown precipitate were formed, and the electrodes became covered with a (partly black) deposit. Gas evolution had almost ceased after 4 hours. An experiment with 3 amps. at 21 cycles gave very similar results—a concentration of 0·27*N* after 2½ hours, considerable electrode corrosion and precipitate formation, and gradual elimination of gas evolution. Before this ceased, it was noticed that much of it was taking place throughout the whole bulk of the electrolyte, not merely at the electrodes. In another experiment, after 4 hours' electrolysis with 1·2 amps. ($n = 6$), the solution was 0·32*N* with respect to hypochlorite. Chlorate was present to the extent of 0·095*N*. It was noticed that, in this case, gas evolution was much stronger at the end of the experiment than in the previous cases, and, at the same time, the electrodes were far cleaner. The addition of free alkali to the original electrolyte lowered the limiting hypochlorite concentration. On the other hand, the addition of 1 g./litre of potassium chromate raised it slightly, concentrations of 0·30—0·31*N* being obtained in three separate experiments, using 1·2 amps. and $n = 6$. Both results are in accordance with those recorded earlier.

Voltage Measurements.—Using the same apparatus, measurements were made of the r.m.s. voltage across the cell under varying conditions of electrolysis. In all cases, an unstirred 3*N*-potassium chloride solution was used, and the cell was cooled by running water. The electrodes were 1 cm. squares of polished and of platinised platinum, in addition to graphite electrodes of as nearly as possible the same area. In all cases, they were placed 1·2 cm. apart. The measurements were made by means of a Duddell thermo-galvanometer, previously calibrated by means of a standard *D.C.* voltmeter. Readings were taken immediately on switching in the current, and repeated at 10-minute intervals during 1 hour. With polished platinum, there was generally a fall during the electrolysis, varying from 1 or 2 centivolts up to several decivolts, comparatively rapid at the start, most noticeable when electrolysis was considerable, and obviously connected with the corrosion or platinisation of the electrodes. With platinised platinum and graphite, at which little or no electrolysis took place, the decreases in voltage noticed were correspondingly less. Occasionally a rise in voltage was observed. Under identical conditions of current and frequency, the cell voltage decreased in the order: polished

platinum>platinised platinum>graphite, represented by (A), (B), and (C) respectively in Table VI, which contains typical figures.

TABLE VI.

Time (mins.) after start.	Voltage across electrodes. $n=6$; $i=0{\cdot}12$ amp.			$n=6$; $i=1$ amp.			$n=48$; $i=1$ amp.		
	(A).	(B).	(C).	(A).	(B).	(C).	(A).	(B).	(C).
0	1·60	1·04	1·10	3·77	3·08	3·23	3·05	2·42	2·22
10	1·58	1·27	1·04	3·63	3·04	3·06	2·95	2·36	2·07
20	1·60	1·32	1·00	3·58	3·02	2·97	2·78	2·34	2·08
30	1·60	1·32	0·98	3·56	3·02	2·97	2·78	2·36	2·08
40	1·60		0·96	3·53		2·97	2·74		2·08
50	1·60		0·83	3·51		2·99	2·59		2·07
60	1·59		0·94	3·51		2·96	2·50		2·06
Electrolysis	Slight	Nil	Nil	Much	Slight	Slight	Slight	Nil	Nil

Owing to the time effect, the data are, in general, unsuited for exact comparison. It is clear, however, that the cell voltage increased both with increased *C.D.* and with diminished frequency. If the last factor were kept constant, more or less linear voltage–current density plots were obtained, which, on extrapolation to zero current, cut the voltage axis at some distance from the origin. These intercepts, which must be regarded as indicative of residual polarisation at the electrodes, were smaller the higher the frequency. But, even with 480 cycles, they corresponded to about 0·5 volt with polished and 0·2 volt with platinised platinum. This last figure must be regarded as showing the linear extrapolation to be unjustified.

Depolarisation by Chlorine at Platinum and Graphite Cathodes.—The lower r.m.s. voltages obtained with graphite as compared with polished platinum electrodes are in agreement with the much smaller degree of electrolysis found when using graphite, and suggest that, in this case, the electrode processes occurring during the anodic and cathodic pulses to a great extent simply reverse one another. The direct-current chlorine over-voltage is known to be greater, during the early stages of electrolysis, at graphite than at smooth platinum (Knobel, Caplan, and Eiseman, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 55), which argues for a slower rate of the reaction $2Cl \longrightarrow Cl_2$, and for a relatively great heaping up of chlorine atoms in the graphite surface layers. Under the conditions of alternating-current electrolysis, these might be expected to ionise during the cathodic pulse, whereas, with a platinum anode, hydrogen ions would be discharged. If, however, the reaction $2Cl \longrightarrow Cl_2$ is slow, so will also be $Cl_2 \longrightarrow 2Cl$, and consequently a graphite cathode depolarised by chlorine should be more easily polarised under the same conditions of *C.D.* than a similar smooth platinum cathode.

Experiments were done to test this view. The cell consisted of a U-tube of wide bore, partly filled with N-hydrochloric acid. In one limb was a platinum anode, in the other a 1 cm.-square cathode of either polished platinum or graphite, half immersed in the electrolyte. Against the cathode pressed the tip of a Luggin capillary, sealed in through the wall of the U-tube, and making connexion, through a bridge of $3N$-potassium chloride, with a normal calomel electrode. By means of a jet sealed into the bottom of this limb, a stream of chlorine gas could be bubbled round the cathode. After the electrolyte had been saturated with chlorine, the static cathode potential was measured, and then a series of continuously increasing small measured currents was passed through the cell, and the potential again observed after each alteration in current. The results are contained in Table VII. The differences observed are very marked, and of the nature anticipated.

TABLE VII.

	Polished platinum cathode.		Graphite cathode.	
Polarising current (milliamps.).	Potential (π_H) (volts).	Change in potential (millivolts).	Potential (π_H) (volts).	Change in potential (millivolts).
0·0	+1·392	—	+1·378	—
0·2	1·390	− 2	1·378	0
1·0	1·383	− 9	1·367	− 11
2·0	1·376	−16	1·350	− 28
3·0	1·371	−21	—	—
4·0	1·366	−26	1·322	− 56
10·0	1·321	−71	1·212	−166

Average Electrode Potentials during Alternating-current Electrolysis.—These measurements were carried out with currents of frequency 20, polished platinum electrodes in $3N$-potassium chloride being used, and a normal calomel electrode. Prior to them, readings were taken with 1 cm.-square electrodes of platinised platinum in N-sulphuric acid, a normal mercurous sulphate electrode being used as reference electrode, and currents of 17 and of 480 cycles being employed. The results indicated that, whilst a static platinised platinum electrode in N-sulphuric acid acts as an air electrode with a potential of about $\pi_H = +0{\cdot}97$ volt, its oxygen content increases and its average potential becomes more positive as electrolysis proceeds. When the current is cut off, the static potential slowly returns to the original air value. Typical results are contained in Table VIII.

Similar observations on the behaviour of the potentials of platinum electrodes in sulphuric acid under the influence of alternating currents have been made by Ghosh (*J. Amer. Chem. Soc.*, 1914, **36**, 2333) and by Vaillant (*Compt. rend.*, 1919, **168**, 768).

TABLE VIII.

Electrode potentials (π_H), volts.

Conditions of measurement.	$n = 480$; $i = 0{\cdot}11$ amp.		$n = 17$; $i = 0{\cdot}15$ amp.	
	π_H.	Change.	π_H.	Change.
Static.	+0·9739	—	+0·9695	—
A.C. on for 0·5 min.	0·9940	+0·0201	1·0211	+0·0516
,, ,, 10 mins.	1·0014	+0·0275	1·0512	+0·0817
,, ,, 20 ,,	1·0046	+0·0307	1·0663	+0·0968
,, ,, 30 ,,	1·0071	+0·0332	1·0749	+0·1054
A.C. off for 10 ,,	1·0046	+0·0307	1·0511	+0·0816
,, ,, 30 ,,	—	—	1·0468	+0·0773
,, ,, 18 hrs.	0·9695	−0·0044	—	—
	No electrolysis.		Traces of gas evolved.	

The behaviour of polished platinum electrodes in $3N$-potassium chloride was, however, different, as is shown in Table IX.

TABLE IX.

Polished platinum electrodes, 1 cm.^{2}. Electrolyte, $3N$-KCl. Frequency, 20 cycles.

Electrode potentials (π_H), volts.

Conditions of measurement.	$i = 0{\cdot}2$ amp.		$= 0{\cdot}3$ amp.		$i = 0{\cdot}5$ amp.	
	π_H.	Change.	π_H.	Change.	π_H.	Change.
Static.	+0·5482		+0·5050		+0·5345	
A.C. on for 2 mins.			0·2443	−0·2607		
,, ,, 10 ,,	0·0424	−0·5058	0·2307	−0·2743	0·3486	−0·1859
,, ,, 20 ,,	0·0481	−0·5001				
A.C. off for 5 ,,			0·7052	+0·2002	0·9540	+0·4195
,, ,, 30 ,,	0·5884	+0·0402	0·7303	+0·2253	0·9832	+0·4487
,, ,, 60 ,,			0·7448	+0·2398		
,, ,, 75 ,,	0·5674	+0·0192				
,, ,, 80 ,,					0·9931	+0·4586
,, ,, 18 hrs.	0·5737	+0·0255				

The average potential measured during electrolysis is seen to be less positive than the static air potential, but to increase with increasing *C.D.* As oxygen is liberated during the electrolysis (although only in traces at those *C.D.*'s used in this series of experiments) and in amounts increasing with, and more rapidly than, the *C.D.*, it is reasonable to assume here also, as with platinised platinum in dilute sulphuric acid, that the average electrode potential corresponds to the average oxygen charge in the electrode during the complete cycle. When the current is cut off, the potential rapidly rises, owing to the hypochlorite in the solution, and to an extent determined by the concentration of the latter. Slow decomposition of the hypochlorite will be accompanied by an ultimate gradual potential fall to the air value. It may be mentioned that Ghosh (*loc. cit.*), using platinum electrodes in hydrochloric acid solutions, also found the potentials to become more negative on polarisation with alternating currents. In this case, however, as no oxidising

agent is formed in solution, the electrode potentials, after electrolysis, simply return gradually to the limiting air potential figures.

Discussion.

The main results of this work are in general agreement with the "fundamental laws" of alternating-current electrolysis formulated by Mengarini (*Electrician*, 1891, 27, 304), *viz.*, that the current efficiency (1) decreases with decreasing *C.D.* and falls to zero below a threshold *C.D.* value, and (2) decreases with increasing frequency and becomes zero above a threshold frequency—these threshold frequencies and *C.D.*'s being functions of one another and also of the particular electrolysis in question. The most interesting feature of Figs. 1 and 3 is the discontinuity shown by the 3*N*-potassium chloride curves at low frequencies when compared with the *N*-potassium chloride curves. These breaks could not be correlated with changes in the electrode surface, and they seem difficult of explanation. Systematic measurements of electrode polarisation, best with the aid of an oscillograph, appear necessary. An increase in *C.D.* also increases the current efficiency of *direct-current* hypochlorite production; but, whereas the favourable effect is here probably connected with the more ready formation of an acid diffusion layer, free from hypochlorite ions, around the anode, in the case of alternating currents it is a question of a relative diminution in the extent to which the anodic and cathodic pulses merely neutralise one another's effects, as a result of discharged ions remaining in or on the electrodes.

The addition of *alkali*, obviously owing to the primary discharge of hydroxyl instead of chlorine ions, has been seen to lower the efficiency of hypochlorite production. This is also the fact in direct-current electrolysis; but, in that case, where higher hypochlorite concentrations are encountered, the cause is rather the destruction of the acid "diffusion layer" mentioned above, and the consequent facilitated anodic discharge of hypochlorite ions. The small effect of the addition of *chromate*, compared with its influence on the course of the direct-current electrolysis, results from the fact that the hypochlorite ions are produced inside, or in the pores of, and not outside, the "cathode diaphragm." For similar reasons, stirring increases the current efficiency, whereas the best results are obtained with direct currents when an undisturbed electrolyte is used.

The limiting hypochlorite concentration observed (about 0·3*N*) is, of course, far lower than that given by a direct current under similar conditions of concentration, current density, and temperature. It corresponds, in fact, roughly to the equilibrium concentration obtained at room temperature with 1·7*N*-sodium chloride, and a *C.D.* of 1·7 amps./dcm.^{2} (Foerster and Müller, *Z. Elektrochem.*,

1903, **9**, 196) whereas, in the present experiments, 3*N*-potassium chloride and a *C.D.* of 1·2 amps./cm.^{2} (at 6 cycles) were employed. As mentioned, chlorate was found to be present, and there is no doubt that, with alternating as with direct currents, the limit reached in the hypochlorite concentration is due to hypochlorite-ion discharge.

The electrode potential data have already been discussed. We will only add that oscillographic measurements appear necessary for their more detailed elucidation.

Summary.

(1) The alternating-current electrolysis of solutions of potassium chloride at room temperature, with polished platinum electrodes, has been investigated.

(2) The influence on the hypochlorite current efficiency of changes in concentration, current density, and frequency have been studied, as have also the effects of adding free alkali or a chromate.

(3) The maximum hypochlorite concentration possible under the conditions of electrolysis has been determined.

(4) Measurements have been made of the average electrode potentials during electrolysis under different conditions.

This work was carried out during the year 1923.

UNIVERSITY OF LONDON,
KING'S COLLEGE. [*Received, September 20th*, 1927.]

CCCXLVIII.—*The Formation of the Sulphites of Azo-compounds.*

By ALBERT THEODORE KING.

THE sodium bisulphite derivatives of azo-compounds, being markedly different in colour from the original azo-compounds, are of great technical interest in relation to commercial azo-dyes. The readiness or otherwise of their formation under various conditions determines the degree of fastness of the dye on wool to stoving (bleaching with sulphur dioxide) and to exposure to town air containing sulphur dioxide.

From preliminary observations that the effect of sulphur dioxide upon azo-compounds is greatly dependent on the conditions under which it is allowed to react, it appeared desirable to examine this reaction further, in relation both to the degree of departure shown, under optimum conditions, from the accepted commercial standards of fastness to stoving and to the influence of constitution and of substituent groups on the ease of sulphite formation.

Spiegel (*Ber.*, 1885, **18**, 1479) prepared a number of these compounds of azo-dyes by reaction of the dyes with warm aqueous or aqueous-alcoholic solutions of sodium hydrogen sulphite, and observed that they were very stable towards dilute acids, but were decomposed by heat and by alkalis into the original dye and alkali sulphite. He regarded them as hydrazo-*N*-derivatives of the general formula $NHX{\cdot}NY{\cdot}SO_3Na$.

Voroschtsov (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 771; 1915, **47**, 1669), on the other hand, regards them as salts of sulphurous esters, *e.g.*, $C_6H_5{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}O{\cdot}SO_2Na$. He assumes that sulphurous acid is added to the naphtholic nucleus in the ketonic form, the product losing a molecule of water. He found that the reaction was characteristic of hydroxyazo-compounds, and that the corresponding aminoazo-compounds, on boiling with aqueous-alcoholic bisulphite, formed the sulphite, not of the aminoazo- but of the hydroxyazo-compound. He also found that the reaction was confined to the azo-derivatives of α- and β-naphthols. These reacted readily, whereas *o*- and *p*-hydroxyazobenzenes and benzeneazo-*o*- and -*p*-cresols underwent no change even on prolonged boiling.

He and his collaborators prepared the sulphites of a number of substituted azonaphthols, but did not make anything more than qualitative observations on their relative ease of formation.

A simple method of measuring the rate of formation of the sulphites of soluble azo-compounds is provided by the fact that these derivatives are very stable not only towards dilute mineral acids, but also towards acidified iodine solution. Thus by running the reaction mixture into excess of acidified iodine solution, and titrating back with thiosulphate, the amount of sulphur dioxide which has become inactive by combination with the azo-compound is readily ascertained. The method is free from the difficulties associated with the estimation of ketone bisulphites (Stewart, J., 1905, **87**, 185).

For the series of experiments to be described, the sodium salts of *p*-sulphobenzeneazo-β-naphthol (Orange II), 4-sulpho-α-naphthaleneazo-β-naphthol (Fast Red A), benzeneazo-β-naphthol-6 : 8-disulphonic acid (Acid Orange GG), and α-naphthaleneazo-β-naphthol-6 : 8-disulphonic acid (Crystal Scarlet) were selected, these having different degrees of fastness to stoving * (1—2, 2—3,

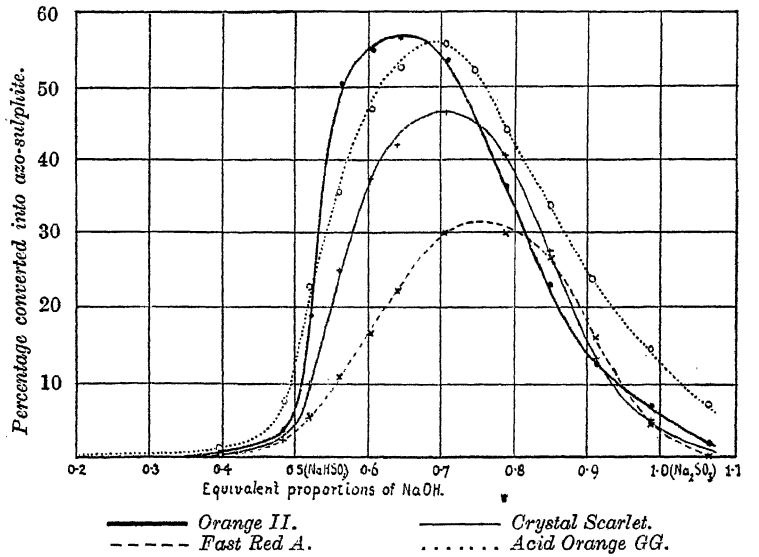
* The standard test for fastness of dyes on wool to stoving is carried out as follows : The dyed sample is soaked in 2% Marseilles soap solution, wrung out, placed in a vessel filled with sulphur dioxide by burning an excess of sulphur, left in for 12 hours, rinsed well in cold water, and dried. The dyes are placed in five classes according to the extent of colour change, class 1 being fast, and 5 the most fugitive.

1, and 2 respectively) and providing some indication of the influence of substitution on the ease of sulphite formation.

The measurements recorded were confined to 2-hour periods of reaction at 25°. Fig. 1 illustrates the percentage converted into sulphite by the equivalent quantity of sulphur dioxide, with various SO_2/NaOH ratios, the reaction mixture corresponding initially to N/50-sulphurous acid.

The most striking variation is shown by Orange II. The reaction is negligible with sulphurous acid alone, and the sharp rise in the

FIG. 1.



percentage of azo-sulphite formed occurs beyond the molecular ratio SO_2/NaOH = 1 (representing the formula $NaHSO_3$), the maximum being with about 1·3 mols. of sodium hydroxide. On either side of this maximum the reaction is extremely sensitive to variation of the SO_2/NaOH ratio.

On the assumption that the reaction consists in direct addition of sodium hydrogen sulphite to the dye to give the hydrazo-*N*-derivative as suggested by Spiegel (*loc. cit.*), $\cdot N{:}N\cdot + NaHSO_3 \longrightarrow \cdot NH\cdot N(SO_3Na)\cdot$, it would be expected that sulphurous acid and caustic soda in equimolecular proportion would effect the most rapid conversion.

Hägglund and Ringborn (*Z. anorg. Chem.*, 1926, **150**, 231) conclude that the addition of bisulphite to ethylenic linkages proceeds according to the similar equation $:C{:}C: + NaHSO_3 \longrightarrow :CH\cdot C(SO_3Na):$.

They found the velocity to depend on the concentration of sodium bisulphite (or the ion HSO_3'), and with normal sulphite there was no action.

Certainly with additional alkali (which readily decomposes azo-sulphites) it would be expected that the reaction would be arrested : $\cdot N{:}N\cdot + Na_2SO_3 + H_2O \rightleftharpoons \cdot NH\cdot N(SO_3Na)\cdot + NaOH$.

With normal sulphite, the reaction is in fact only slight (Fig. 1), although a small excess of sodium hydroxide beyond this proportion is needed to inhibit the reaction completely.

The above optimum ratio of greater than unity accords with the view that the hydroxy-group is participating in the reaction, and that theoretically the most rapid conversion would occur with a further molecular proportion of alkali, but that actually this is balanced by the simultaneous decomposing action of the latter.

It is known (Stewart and Baly, J., 1906, 89, 489) that the bisulphite compounds of ketones are formed much more rapidly in the case of tautomeric compounds like acetoacetic ester, the reactivity being presumed to be inherent, not in the carbonyl group itself, but in its tautomeric character, which is governed by the action of the adjacent groups upon the carbonyl radical.

Evidence has been advanced, principally by Goldschmidt and Löw Beer (*Ber.*, 1905, 38, 1908), refuting the quinonoid structure of *p*-hydroxyazo-compounds, but there is still a conflict of opinion on this point (compare Puxeddu and Germain, *Gazzetta*, 1922, 52, i, 216) and Voroschtsov's view can be supported, even accepting the azophenolic structure, by assuming a similarly tautomeric hydroxyl group. This may also be the determining factor in the velocity of reaction, as Stewart and Baly maintain in the case of ketones. In the tautomerism of the latter, however, alkali favours the enol form, and the precise rôle of the excess of alkali above mentioned in accelerating the formation of azo-sulphites is not at present clear.

So far as is indicated by the four azo-β-naphthols examined, the sulphonaphthalene group obviously has a retarding effect compared with the benzene derivative, and the benzeneazonaphtholdisulphonate also is more reactive than the corresponding naphthaleneazonaphtholdisulphonate, but any generalisation must be deferred pending results over a wider range of azo-derivatives.

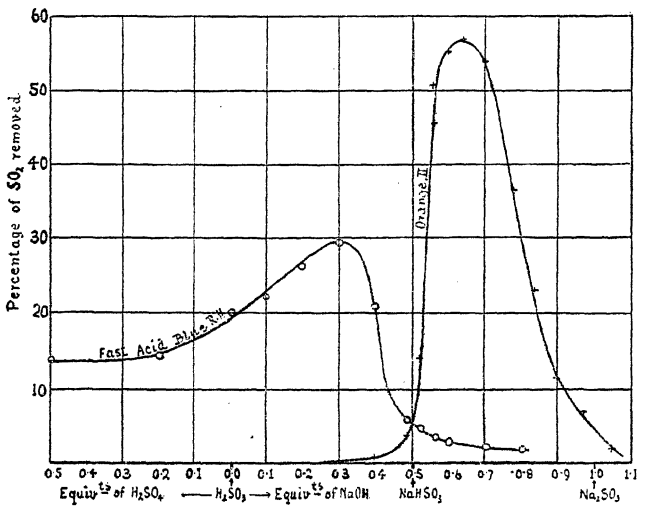
This preliminary series is, however, sufficient to illustrate both the varying reactivity of azo-compounds to sulphur dioxide under different conditions and also the anomalous behaviour at times encountered with dyes scheduled as of good fastness to sulphur dioxide under the special conditions of the stoving test, owing to their unsuspected sensitiveness to this reagent under favoubrale

conditions which can in various ways be fortuitously realised in practice.

As previously mentioned, the formation of azo-sulphites is not general with azo-dyes. The examples above were selected on account of their observed susceptibility and are all β-naphthol derivatives. The α-naphthol derivatives would appear to be generally less sensitive, and similar work on these is projected.

In addition, a third type, principally aminoazo-compounds, does not, according to Voroschtsov, give bisulphite derivatives, but either through fission or other form of decomposition is destroyed by bisulphite and is thus not regenerated by subsequent treatment

FIG. 2.



with caustic soda. As an example of such compounds, the sodium salt of 3 : 6-disulpho-8-hydroxy-α-naphthaleneazo-α-naphthylphenylamine-8-sulphonic acid (Fast Acid Blue RH),

$$OH\cdot C_{10}H_4(SO_3Na)_2\cdot N{:}N\cdot C_{10}H_5(SO_3Na)\cdot NHPh,$$

was investigated. This is very fugitive to stoving, turning eventually yellow, and is entirely different in behaviour towards sulphur dioxide from the sulphite-forming azo-compounds (Fig. 2). The extent of reaction in the 2-hour period employed is most marked with about 0·3 equivalent of alkali, and under the optimum sulphite-forming conditions the dye scarcely reacts at all.

Thus the foregoing results indicate that more precise information on the reactivity of sulphur dioxide towards the various types of azo-dyes is desirable from both the theoretical and the practical aspect, and further work is in progress with this end in view.

EXPERIMENTAL.

The dyes in question readily lend themselves to purification. Orange II, already practically pure in commercial form, was recrystallised twice from 90% ethyl alcohol. Acid Orange GG, Crystal Scarlet, and Fast Red A were first separated from inorganic salts by solution in pyridine and reprecipitation with ether; the Fast Red A was then recrystallised from amyl alcohol, and the other two from 90% ethyl alcohol. Their purity was checked by evaluation with titanous chloride, which gave Orange II 99·93%, Acid Orange GG 100·3%, Crystal Scarlet 99·0%, and Fast Red A 99·1%.

Preparation of Azo-sulphites.—The sulphites of the above-mentioned azo-compounds were obtained by stirring the powdered dye into excess of concentrated sodium bisulphite solution, gently warming the liquid, and keeping it over-night. The bisulphite solution is conveniently made by adding 10% sodium hydroxide solution to commercial bisulphite solution (20% SO_2) until the latter reacts only faintly acid to litmus paper. The ease of isolating the azo-sulphite varies with the azo-compound employed.

Sodium 4-*Sulpho*-α-*naphthaleneazo*-β-*naphthyl Sulphite* (Bisulphite Compound of Fast Red A).—The reaction mixture was filtered, and the solution saturated with sodium chloride. The precipitate thus obtained was twice again salted out from aqueous solution and was then deposited from aqueous-alcoholic solution, by gradual addition to ether, as a reddish-orange, crystalline, hygroscopic powder (Found: S as sulphite, 6·65. Calc. for $C_{20}H_{12}O_6N_2S_2Na_2$: S as sulphite, 6·6%).

The sulphite sulphur was estimated by adding the substance, dissolved in excess of air-free aqueous sodium hydroxide, to excess of acidified iodine solution and titrating the residual iodine with thiosulphate. Estimations of total sulphur by the Carius method gave low results, presumably through incomplete breaking down of the sulphonic group.

Sodium p-*Sulphobenzeneazo*-β-*naphthyl Sulphite* (Bisulphite Compound of Orange II, commercial name "Narceine").—The reaction mixture deposited a portion of the azo-sulphite on cooling. The bulk was separated by adding a little sodium chloride. It was again salted out and then recrystallised by cooling a warm concentrated aqueous solution, being thus obtained in buff-yellow crystals (Found: S as sulphite, 7·3. Calc. for $C_{16}H_{10}O_6N_2S_2Na_2$: S, 7·3%).

Sodium Benzeneazo-6 : 8-*disulpho*-β-*naphthyl Sulphite* (Bisulphite Compound of Acid Orange GG).—This substance, which is not precipitated from its aqueous solution by sodium chloride, was

isolated by adding to the reaction mixture twice its volume of alcohol, which left it in solution together with some sodium bisulphite. The solution was evaporated to small bulk at a low temperature and fractionally precipitated by careful addition of alcohol. The inorganic salt was precipitated first, and the azo-sulphite was obtained, by pouring the filtrate slowly into alcohol–ether, in fairly pure condition as a canary-yellow, hygroscopic powder.

Sodium α-naphthaleneazo-6 : 8-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Crystal Scarlet) was isolated by the method described under Acid Orange GG and obtained as a reddish-orange powder deliquescing in air.

Stability of Azo-sulphites towards Acidified Iodine Solution.—The azo-sulphite (0·5 g.) was added to 25 c.c. of acidified iodine solution and kept for 24 hours. The blank required 21·9 c.c. of thiosulphate, and the azo-sulphites required: Fast Red A (A) 21·9 c.c., Acid Orange GG (B) 21·9 c.c., Orange II (C) 20·9 c.c., Crystal Scarlet (D) 19·6 c.c. The low results for (C) and (D) were mainly due to contamination with inorganic sulphite, since it was found that by adding iodine to the azo-sulphite in solution until the latter reacted to starch paper, and then pouring the mixture into 25 c.c. of acidified iodine, the thiosulphate figures were 21·54 and 21·4 c.c. respectively. The reaction, if any, after 24 hours' contact with iodine is thus so small as to warrant the accuracy of the method described below of estimating mixtures of alkali- and azo-sulphites.

Determination of Azo-sulphite Formation.—The purified anhydrous azo-compounds were dissolved in boiled-out water and made up to *M*/40-solutions, 20 c.c. thus being equivalent to 10 c.c. of *N*/10-sulphurous acid. To 20 c.c. of each dye solution were added first the desired volume of *N*/10-sodium hydroxide, then water (to make up eventually to 50 c.c.), and finally the sulphurous acid, the solution thus being *N*/50 as regards both azo-compound and sulphite. The reaction mixtures were contained in stoppered tubes of slightly greater capacity, to reduce air-oxidation of the sulphur dioxide to the minimum. After remaining 2 hours in a water-bath at 25°, the contents of the tube were washed out into excess of acidified iodine solution, which was thereafter titrated with thiosulphate. The highly coloured solutions necessitated the use of starch as indicator. The end-point was very sharp.

Preparation of the Sulphurous Acid Solution.—In the initial experiments concordant results could not be obtained owing to the changing strength of the sulphurous acid and simultaneous formation of free sulphuric acid, each of which changed the SO_2/NaOH ratio and thus greatly affected the rate of reaction. To obviate this, a Winchester filled with boiled-out water was allowed to cool

with wash-bottles of alkaline pyrogallol attached, and sulphur dioxide from a syphon was passed in to give an approximately $N/10$-solution. A self-filling burette was fitted so that air entering by displacement was deprived of oxygen by alkaline pyrogallol; the absorption bottles were cut off except during the running off from the burette, to avoid any loss of sulphur dioxide from the inside atmosphere by absorption in the pyrogallol. This solution remained practically constant in strength throughout the whole series of analyses. It gave a normality of 0·1423 as sulphurous acid, and 0·1444 as total sulphur, estimated as barium sulphate, the free sulphuric acid present thus involving the small correction of 0·15 c.c. to the calculated volumes of $N/10$-sodium hydroxide added.

Tabulated Results.

C.c. of 0·103N-NaOH added (expressed as c.c. of $N/10$-NaOH and corrected).	SO_2 combined (c.c. of $N/10$-soln.).			
	A.	B.	C.	D.
—	(−0·05)	(−0·03)	0·05	0·10
3·97	(−0·15)	0	0·07	0·13
4·86	0·35	0·78	0·37	0·16
5·21	0·55	1·81	1·90	1·0
5·62	1·10	3·58	5·05	2·5
6·03	1·65	4·68	5·50	3·79
6·44	2·20	5·38	5·65	4·20
7·06	3·00	5·60	5·35	4·65
7·47	—	5·24	—	—
7·88	3·00	4·43	3·65	4·05
8·50	2·70	3·43	2·30	2·75
9·12	1·60	2·43	1·25	1·30
9·86	0·45	1·46	0·70	0·45
10·66	0	0·73	0·20	0·2

The percentage of sulphur dioxide combined is obtained by multiplying the number of c.c. of $N/10$-solution by 10.

The curves plotted from these values are shown in Fig. 1. The values for sulphurous acid have been disregarded, since even after 24 hours no reaction could be detected with certainty; also no correction has been made for any loss of sulphurous acid by oxidation, blank determinations having shown that the loss during 2 hours, although increasing slightly with alkalinity, involved no serious error.

Reaction with Fast Acid Blue RH.—In this case, the deep blue colour obscures the colour change of starch in the solution, but by using starch as external indicator the end-point can be determined with fair precision.

The following results were obtained, the same quantities of dye and sulphurous acid being used as before, for a 2 hours' period of reaction (see Fig. 2):

N/10-H_2SO_4 added (c.c.).	% SO_2 combined.	N/10-NaOH added (c.c.).	% SO_2 combined.
5	14·2	3	29·5
2	14·5	3·98	21·0
		4·86	6·0
H_2SO_3 alone.	20·0	5·21	5·0
N/10-NaOH added (c.c.).		5·62	3·5
		6·03	3·0
1	22·0	7·06	2·3
2	26·5	8·1	2·3

BRITISH RESEARCH ASSOCIATION FOR THE WOOLLEN AND WORSTED INDUSTRIES, TORRIDON, HEADINGLEY, LEEDS. [*Received, August 17th*, 1927.]

CCCXLIX.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR'N *in Aromatic Substitution. Part VIII. The Nitration of* 4-n-*Butoxyanisole.*

By JOHN CLARKE, ROBERT ROBINSON, and JOHN CHARLES SMITH.

A STUDY of the nitration of 2-alkyloxyanisoles (Part I, Allan and Robinson, J., 1926, 376) showed that the directive powers of some alkyloxy-groups are in the order EtO > *n*-PrO > *n*-BuO > MeO, whilst in the nitration of 4-alkyloxyanisoles the order found was *n*-PrO > EtO > MeO (Part III, Robinson and Smith, J., 1926, 392). We have now determined the directive power of the *n*-butoxy-group in the quinol series and it is appreciably greater (186) than that of the *n*-propoxy-group (180). In view of the high yields obtained in the nitrations, the fact that only two monosubstituted derivatives are possible, and the precautions observed in applying the method of thermal analysis, we have little doubt that this difference is real and lies beyond the limits of experimental error. The small fall in the directive powers in the pyrocatechol series in passing from *n*-PrO (128) to *n*-BuO (123) and the small corresponding rise (180—186) in the quinol series may now be disregarded, if desired, in favour of a comparison of EtO and *n*-BuO in both series. In the pyrocatechol series, we find EtO = 135 and *n*-BuO = 123, and in the quinol series, EtO = 163 and *n*-BuO = 186. A theoretical explanation embracing these phenomena was advanced in Part IV of this investigation (Allan, Oxford, Robinson, and Smith, J., 1926, 402), and the result for *n*-BuO is in agreement with its requirements.

EXPERIMENTAL.

Purification of Materials.—The methyl alcohol was free from acetone and distilled completely within 0·1°. The acetic acid was distilled and repeatedly frozen until the m. p. was 15·8—16·0°.

Pure nitric acid of constant b. p. was distilled (d 1·41). A good specimen of *n*-butyl alcohol was washed with dilute sulphuric acid and sodium bisulphite solution, and then boiled for 1·5 hours with 20% aqueous sodium hydroxide; it was separated, dried with potassium carbonate, and later with barium oxide. On distillation through an efficient column, a fraction, b. p. 117·6°/760 mm., $d_4^{25°}$ 0·8056, was obtained (Brunel, Creashaw, and Tobin, *J. Amer. Chem. Soc.*, 1921, **43**, 561, give b. p. 117·71°/760 mm. and $d_4^{25°}$ 0·8057). This specimen was unchanged by further attempted purification, as mentioned below, and was employed in our work. The alcohol was converted into *n*-butyl salicylate and subsequently treated as described by Orton and Jones (J., 1919, **115**, 1198); the recovered material had b. p. 117·6°/762 mm. and $d_4^{25°}$ 0·8056; $d_4^{20°}$ 0·8094; $d_4^{15°}$ 0·8132; $d_{14·4}^{14·4°}$ 0·8141. A second portion was converted into *n*-butyl gallate, which crystallised readily from toluene in needles, m. p. 143—144° (Found: C, 58·3; H, 6·2. Calc. for $C_{11}H_{14}O_5$: C, 58·4; H, 6·2%). Subsequent to the completion of our work, we found that *n*-butyl gallate had been described by Christiansen (*J. Amer. Chem. Soc.*, 1926, **48**, 1358), who gives the m. p. 133—134°. This derivative was hydrolysed by means of aqueous sodium hydroxide in an atmosphere of hydrogen, and the recovered alcohol had b. p. 117·5°/760 mm., $d_4^{20°}$ 0·8094. Commercial *n*-butyl alcohol (600 c.c.) esterified with gallic acid (250 g.) gave about 200 g. of the ester, m. p. 141—143°, and after one crystallisation from toluene the m. p. was 142—144°. The alcohol obtained on hydrolysis all distilled at 117·9—118·1°/769 mm. (117·6—117·8°/760 mm.) and had $d_4^{20°}$ 0·8099. This experiment seemed to show that the process of purification we contemplated was satisfactory, but it cannot be trusted in all circumstances, as the following observations clearly proved. In the first place, a mixture of *n*-propyl and *n*-butyl alcohols was esterified with gallic acid and the ester isolated had m. p. 148—149°, or by a different method, m. p. 150—151°. Recrystallisation from toluene gave a crop, m. p. 152—153°, and another, m. p. 151—153°. We then prepared *n*-propyl gallate, m. p. 147—148° (see below), and found that a mixture of equal quantities of *n*-propyl and *n*-butyl gallates, mixed dry, had m. p. 152—154°, with no sign of sintering at 143° or 147°. On cooling, the liquid crystallised at 145°; it then fused again at 152—154°. This is, therefore, an addition to the small number of recorded cases of binary mixtures that melt at a higher temperature than either of the components.

n-Butyl bromide was prepared by the method of Kamm and Marvel (*J. Amer. Chem. Soc.*, 1920, **42**, 299) and had b. p. 101·2°/759 mm., $d_4^{20°}$ 1·2764.

n-*Propyl Gallate*.—A mixture of propyl alcohol (50 c.c.), sulphuric acid (1 c.c.), and gallic acid (17 g.) was boiled under reflux for 4 hours (in the case of *n*-butyl gallate, the period of heating should not exceed 3 hours) and then concentrated somewhat by distillation under diminished pressure. The residue crystallised, and was thoroughly washed with water and dried at 80°. The almost colourless crystals were practically pure and the substance crystallised from water in long needles, m. p. 147—148° (Found: C, 56·7; H, 5·7. $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%). This ester is rather more readily soluble in water than is *n*-butyl gallate, whilst it is the more sparingly soluble of the two in toluene.

2-*Nitro*-4-n-*butoxyanisole*.—Potassium (3·9 g.) was dissolved in methyl alcohol (100 c.c.), and after the successive introduction of 3-nitro-4-methoxyphenol (16·9 g.) (Part III, *loc. cit.*) and *n*-butyl bromide (15 c.c.), the mixture was refluxed for 3 hours; as the colour was still red, a further 5 c.c. of butyl bromide were added and the boiling was continued for 2 hours. The greater part of the solvent was removed by distillation under diminished pressure, and an ethereal solution of the residue was twice washed with aqueous sodium carbonate, thrice with water, and then dried. After removal of the ether, the yellow oil distilled at 143°/1 mm. and had f. p. 12·4°, m. p. 12·5° (yield, 17 g. or 76%). After one recrystallisation from methyl alcohol at — 15° (the filter was cooled by a jacket containing a mixture of solid carbon dioxide and ether) and removal of the adherent solvent at 110° in a vacuum, the values observed were: f. p. 13·1°, m. p. 13·25°, $n_D^{14\cdot4°}$ 1·5382 (Found: C, 58·6; H, 6·7. $C_{11}H_{15}O_4N$ requires C, 58·7; H, 6·7%). The f. p. and m. p. were not raised by a further recrystallisation. A second preparation (yield, 81%) had f. p. 12·6°, m. p. 12·7°, raised on recrystallisation to the constant values 13·15° and 13·20°, respectively; $n_D^{14\cdot4°}$ 1·5382.

3-*Nitro*-4-n-*butoxyanisole*.—A solution of potassium (7·8 g., 0·92 mol.) in *n*-butyl alcohol (100 c.c.) and 2-nitro-4-methoxyphenol (33·8 g., 1 mol.) (Part III, *loc. cit.*) were mixed, and after the addition of *n*-butyl bromide (21 c.c.) the mixture was refluxed for 20 hours with the gradual further addition of *n*-butyl bromide (29 c.c.). After cooling, the brown liquid was decanted from the potassium bromide, which was washed with a little butyl alcohol, and the solvent completely removed by distillation under diminished pressure. An ethereal solution of the residue was washed with aqueous sodium carbonate and water, then dried and distilled. A pale yellow oil (18·75 g.), b. p. 137°/1 mm., was obtained and 2-nitro-4-methoxyphenol (11·5 g.) was recovered from the alkaline extracts. A second preparation on half the scale gave a rather larger yield (53% calculated on the potassium) of an identical

product, and both specimens, after being crystallised thrice from methyl alcohol at — 50°, gave long, yellow needles, which, after separation and complete removal of adhering solvent at 110° in a vacuum, had m. p. — 9·7°, $n_D^{14\cdot0°}$ 1·5358 (Found: C, 58·6; H, 6·8. $C_{11}H_{15}O_4N$ requires C, 58·7; H, 6·7%). The m. p.'s were determined as follows: the substance in a tube was cooled to — 20° and stirred until crystallisation began; it was then placed in an air-jacket fitted into a transparent Dewar vessel containing brine at — 12°. While the cold bath was stirred occasionally and the nitro-compound regularly (and vigorously on account of the viscosity of the material), the temperature gradually rose until the thermometer in the nitro-compound registered — 9·7° and remained steady for some minutes.

Mixtures of 3-*Nitro*-4-n-*butoxyanisole and* 2-*Nitro*-4-n-*butoxyanisole.*—The mixtures were rather viscous below 0°, and reproducible values could only be obtained over the composition range given below. It was found that characteristic values could best be assigned by taking the mean of the f. p. and m. p. of each mixture. A series of 4—6 determinations was made in each case as in the example: Composition, 94·3% of 2-nitro-4-*n*-butoxyanisole; f. p.'s, 11·40°, 11·30°, 11·35°, 11·40°; m. p.'s, 11·50°, 11·50°, 11·45°, 11·45°; mean, 11·42°. It was found necessary to eliminate water from the mixtures every 2—3 hours and also after any operation involving dismantling. The water did not actually depress the f. p.'s, but it retarded crystallisation. It was evaporated at 110°/20 mm. in a stream of dry air introduced through a fine tube; care was taken not to lose any of the material adhering to this tube or to the silver wire stirrer and thermometer—during temporary removal, these details were protected from dust. For the determination of the f. p.'s and m. p.'s, the apparatus mentioned above was employed; the temperature of the bath in the Dewar vessel could be raised or lowered by admission of water at different temperatures from reservoirs. In the first place, the m. p. was roughly determined while the bath was kept at a temperature 0·5—1° lower than that of the nitro-compound. The tube was then removed from the air-jacket and allowed to warm until almost all the solid had melted; it was then cooled to 2° below the m. p. and stirred to initiate crystallisation. After the tube was replaced in the apparatus, the bath was kept at 1° below the m. p., and the f. p. determined. As a rule, the temperature remained constant for some minutes. The temperature of the bath was then raised to about 0·5° below the f. p. and stirring continued, so that heat might enter and cause the mixture to melt. In this way, the temperature of the mixture usually rose 0·1—0·15° and remained steady at the m. p. until

almost all the solid had disappeared; a sudden rise supervened. The following f. p.–m. p. means were determined, the first number of each pair indicating the % of the 2-nitro-isomeride in the mixture: 100, 13·20°; 94·3, 11·42°; 86·4, 9·12°; 82·65, 7·88°; 79·58, 6·95°; 77·08, 6·00°; 73·77, 4·90°; 71·94, 4·09°; 69·06, 3·00°. The corresponding graph is a smooth curve.

4-n-*Butoxyanisole.*—Pure quinol monomethyl ether (6·2 g.) was added to a solution of sodium *n*-butoxide (from 1·15 g. of sodium) in *n*-butyl alcohol (30 c.c.), and after the introduction of *n*-butyl bromide (6·5 c.c.) the mixture was refluxed for 2 hours. After removal of the solvent at 50—70° in a vacuum, the product was steam-distilled and crystallised in contact with ice-water (yield, 7·6 g. or 85%). The substance crystallised from methyl alcohol containing a little water in large, pearly plates, m. p. 24·5—25·5° (Found: C, 73·4; H, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%). This ether was also satisfactorily obtained by the use of sodium methoxide in acetone solution.

Nitration of 4-n-*Butoxyanisole.*—4-*n*-Butoxyanisole (2·0 g.), dissolved in acetic acid (4 c.c.), was nitrated by means of nitric acid (1·03 g.) in acetic acid (1 c.c.), and the product isolated as in the case of the nitration of 4-*n*-propoxyanisole (Part III, *loc. cit.*). The products were, however, washed with sodium carbonate instead of with the bicarbonate in order to avoid effervescence; yields, (*a*) 96·4%, (*b*) 97·2%, (*c*) 97·4% (Found: N, 6·2. Calc.: N, 6·2%). Specimens (*c*) and (*d*) were isolated without the aid of methyl alcohol, the washed oil being siphoned through a Pregl micro-filter into the freezing-point tube. Specimen (*b*) was orange-yellow and was not further examined, whilst (*c*) was specially prepared for analysis; (*a*), (*c*), (*d*), and (*e*) were clear, pure yellow oils. The following table displays the results; 6—8 determinations of each f. p. and m. p. were made.

Specimen.	Mixture taken, g.	2-Nitro-isomeride added, g.	F. p. (mean).	M. p. (mean).	Mean.	% of 2-nitro-isomeride indicated.	% of 3-nitro-isomeride in nitration product.
(*a*)	1·0052	1·4758	4·72°	4·88°	4·80°	73·7	64·9
		1·9920	6·41	6·53	6·47	78·3	64·7
(*c*)	0·5993	1·0141	5·46	5·59	5·53	75·7	65·4
		1·3133	6·82	6·98	6·90	79·6	65·1
(*d*)	0·5027	0·8216	5·35	5·46	5·41	75·35	64·9
							Mean 65·0

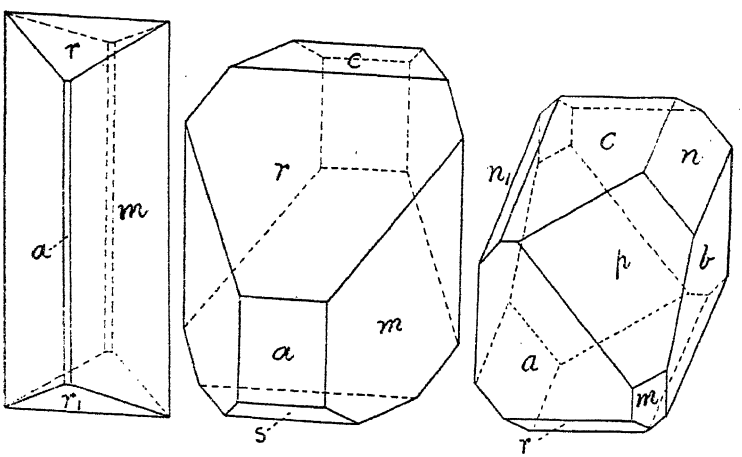
Hence the directive power of *n*-BuO is 186 (MeO = 100).

In order to determine the effect of the process of isolation on the composition of the nitration product the following experiment was carried out. The product (*d*) (1·25 g.) was dissolved in acetic acid (3 c.c.), cooled to 0°, and a mixture of acetic acid (3 c.c.) and nitric

acid (0·7 g.) added. The concentrations of the nitro-compounds were then exactly half of those at the end of a normal nitration, and dilution and washing were carried out in the normal way. When the last water layer had been removed, the entire process was repeated; the specimen was thus subjected to a process which should produce four times the normal change. The weight of re-washed oil was 1·172 g. (loss, 6·24% or 1·6% for the normal process). 0·5029 G. of this with 2-nitro-4-*n*-butoxyanisole (0·8215 g.) had f. p. 5·37°, m. p. 5·48°, mean, 5·42°. Hence the loss is mechanical and involves no change in composition.

Crystallographic Measurements.—Mr. H. E. Buckley of the Crystallography Department of this University submits the following reports relating to substances described in Part III (*loc. cit.*).

FIG. 1. FIG. 2. FIG. 3.



2-Nitro-4-methoxyphenol. The crystals (Fig. 1) are of a short-prismatic habit and deep orange colour. Symmetry: Monoclinic (pseudo-orthorhombic). $a : b : c = 1{\cdot}0234 : 1 : 0{\cdot}5732$; $\beta = 90°$. Forms developed: $m(110)$, $r(101)$, $r_1(10\bar{1})$, $a(100)$, and occasionally $l(210)$, $n(120)$, $s(320)$, and $t(230)$.

	Angles observed.	Calc.
110—1$\bar{1}$0	91° 21′ (8)	—
110—101	70° 1′	—
100—101	60° 44′	60° 45′
110—320	11° 32′	11° 21′
110—210	18° 35′	18° 34½′

Cleavage parallel to $r(10\bar{1})$ perfect.

Double refraction appears to be very strong, the interference figure being practically in the plane of cleavage 101. There is a slight pleochroism, varying from orange through yellow to pale green.

2-*Nitro*-4-*ethoxyanisole* (Fig. 2). Symmetry: Monoclinic [holohedral]. $a : b : c = 1{\cdot}431 : 1 : 1{\cdot}569$; $\beta = 77° 23'$. Forms developed: $a = 100$, $c = 001$, $r = 101$, $s = 10\bar{1}$, $m = 110$, and $p = 111$ (infrequent).

	Angles observed.	No. measured.	Limits.	Calc.
100—001	77° 2½′	7	76° 58′—77° 8′	—
100—110	53° 42′	11	53° 35′—53° 58′	—
101—001	35° 52½′	6	35° 48′—35° 56′	—
101—100	41° 10′	6	40° 59′—41° 16′	41° 10′
100—10$\bar{1}$	55° 40′	6	55° 36′—55° 47′	55° 39′
110—10$\bar{1}$	70° 26′	7	70° 14′—70° 34′	70° 30½′
110—101	63° 26½′	11	63° 10′—63° 44′	63° 32′
110—001	82° 18′	8	82° 6′—82° 36′	82° 26′
001—111	50° 57′	3	50° 41′—51° 15′	51° 10′

2-*Nitro*-4-n-*propoxyanisole*. System: Triclinic (pinacoidal). $a : b : c = 0{\cdot}7831 : 1 : 1{\cdot}030$; $\alpha = 92° 54'$, $\beta = 55° 32'$, $\gamma = 87° 12'$. Forms developed: $a = 100$, $b = 010$, $c = 001$, $m = 110$, $r = 10\bar{1}$, $n = 011$, $n_1 = 0\bar{1}1$, and $p = 111$. The habit is often tabular on the 111 face (Fig. 3).

Angular elements.	Observed.	No. measured.	Limits.
a—p (100—111)	31° 3′	4	31° 0′—31° 5′
a—b (100—010)	88° 33′	3	—
a—c (100—001)	55° 48′	8	55° 34′—56° 11′
n—p (011—111)	31° 58′	4	31° 56′—32° 3′
n—b (011—010)	50° 35′	4	50° 33′—50° 39′

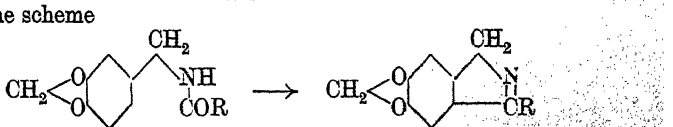
The crystals are of considerable interest in that they exhibit remarkably well their anorthic optical properties. The first mean line, which varies a little for different colours, is nearly normal to 111, on which the crystal is tabular, and the optic axial plane for the sodium yellow line is turned through practically a right angle from that for the mercury violet line.

THE UNIVERSITY, MANCHESTER. [*Received, August 20th*, 1927.]

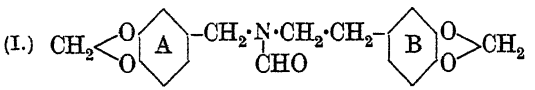
CCCL.—*Facile Ring-closure to a Derivative of Dihydro*isoquinoline *contrasted with the Difficulty of Analogous Formation of a Derivative of* iso*Indole.*

By JACQUES MALAN and ROBERT ROBINSON.

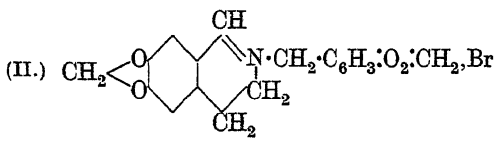
EXAMPLES of the production of *iso*indole derivatives by a reaction analogous to the Bischler–Napieralski synthesis of dihydro*iso*quinolines have not been recorded, and our own attempts to dehydrate aceto- and benzo-piperonylmethylamides in accordance with the scheme



have been fruitless. Such negative results are often attributable to various fortuitous causes, *e.g.*, unsuitable conditions, impure or too pure reagents, but, in the course of some preliminary synthetical experiments in the *iso*quinoline group of the alkaloids, we encountered a case free from such objections, and one that proves that the difficulty experienced in closing the *iso*indole ring is not fortuitous. The complex formamide (I) might give either a five-membered or a six-membered heterocyclic ring on dehydration, but, actually, a substance containing the latter is the only product of the action of phosphoryl chloride on the amide. The constitution of the

(I.) 

quaternary ammonium salt obtained was proved by an independent synthesis. Interaction of methylenedioxydihydro*iso*quinoline and piperonylmethyl bromide yielded the bromide (II), which was

(II.) 

convertible into a *picrate*, *pseudo-cyanide*, and an *anhydro-base-nitromethane* derivative identical, each to each, with the same series obtained from (I).

One of the factors controlling the direction of the ring closure is doubtless the field associated with the positive charge of the nitrogen atom, which is probably in the ammonium state under the conditions of the reaction. This field is evidently more intense over nucleus (A) than over nucleus (B), and as it should tend to inhibit union of the nuclear carbon with that of the $-CHO$ group, itself kationoid, an adequate explanation of the formation of the *iso*quinoline derivative is forthcoming. For a similar reason, the formation of *iso*quinoline derivatives from substances of the form $Ar{\cdot}CH_2{\cdot}CH_2{\cdot}N{\cdot}CO{\cdot}$ should be more facile than from substances of the form $Ar{\cdot}CH_2{\cdot}N{\cdot}CH_2{\cdot}CO{\cdot}$, provided that the carbonyl group has an approximately equal reactivity in each case. Several illustrative cases have been recorded (Mannich and Kuphal, *Arch. Pharm.*, 1912, **250**, 539).

Experimental.

Piperonylmethylamine Derivatives.—Piperonylmethylamine, b. p. 172°/50 mm., was obtained in 70% yield by the reduction of piperonaldoxime by means of zinc dust in boiling 50% acetic acid solution (Mannich and Kuphal, *Ber.*, 1912, **45**, 314). The *chloroplatinate* crystallises from much hot water in orange needles [Found :

Pt, 27·7. $(C_8H_9O_2N)_2,H_2PtCl_6$ requires Pt, 27·6%]. The *picrate* crystallises from water in yellow needles, m. p. 198°. *Piperonylmethyltrimethylammonium iodide*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}NMe_3I$, obtained by the action of an excess of methyl iodide on the base, crystallises from alcohol in minute, yellow prisms, m. p. 219° (decomp.) (Found: C, 41·0; H, 5·1; I, 38·7. $C_{11}H_{16}O_2NI$ requires C, 41·1; H, 5·0; I, 39·2%).

Benzylidenepiperonylmethylamine, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}N{:}CHPh$, readily obtained by condensation of the base with benzaldehyde, crystallises from aqueous alcohol in colourless needles, m. p. 51—52° (Found: C, 75·5; H, 5·7. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4%); its *picrate* crystallises from alcohol in light yellow needles, m. p. 206°.

2-*Carbomethoxyveratrylidenepiperonylmethylamine*,

$$CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}N{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CO_2Me,$$

is obtained by heating methyl opianate and piperonylmethylamine in molecular proportion at 150°. It crystallises from alcohol in flocculent masses of colourless, microscopic needles, m. p. 181° (Found: C, 63·2, 63·8; H, 4·8, 5·0; N, 4·1. $C_{19}H_{19}O_6N$ requires C, 63·8; H, 5·0; N, 4·1%). An interesting transformation of this substance occurs under the influence of sodium methoxide in hot methyl-alcoholic solution. The elements of methyl alcohol are eliminated and the neutral product crystallises from methyl alcohol in glistening, hexagonal prisms, capped with pyramids, m. p. 159° (Found: C, 66·1, 66·4; H, 4·9, 4·9; N, 4·5. $C_{18}H_{15}O_5N$ requires C, 66·5; H, 4·6; N, 4·3%). The most natural hypothesis is that this substance is 4-*hydroxy*-5:6-*dimethoxy*-3-*piperonyl*isoquinoline, but its properties are somewhat at variance with such a view. For example, the action of boiling methyl iodide gives rise to an *iodide*, m. p. 172° (Found: C, 36·8, 36·3; H, 4·1, 4·0; I, 41·7; and, for instance, $C_9H_{12}O_2NI$, piperonylmethylmethylamine hydriodide, requires C, 36·8; H, 4·1; I, 43·3%). Evidently the molecule has been broken up, and this is difficult to reconcile with the *iso*quinoline formulation. A by-product in the preparation of piperonylmethylamine is *di(piperonylmethyl)amine*, b. p. 230°/50 mm., which crystallises from alcohol in silky needles, m. p. 114°. The foregoing experiments were made by Miss B. Dobson in these laboratories in 1910.

Acetopiperonylmethylamide crystallises from benzene in colourless needles, m. p. 103° (Found: C, 62·2; H, 5·3. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7%). Attempts to dehydrate this substance, and similar trials with benzopiperonylmethylamide, m. p. 117° (Mannich and Kuphal, *loc. cit.*), by means of phosphoryl chloride, phosphoric anhydride, sulphuric acid, zinc chloride and stannic chloride failed, the amides being either recovered unchanged or converted into dark violet substances that could not be purified.

It is relevant to mention here that the ring closure of *phenacyl veratrate*, $C_6H_3(MeO)_2 \cdot CO \cdot O \cdot CH_2 \cdot COPh$, to an *iso*coumarin derivative has been unsuccessfully attempted. The ester is obtained in good yield by the interaction of ω-bromoacetophenone and silver veratrate in boiling alcoholic solution. It crystallises from alcohol in well-defined, elongated prisms, m. p. 122° (Found: C, 68·0; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

Piperonylmethyl-β-piperonylethylamine,

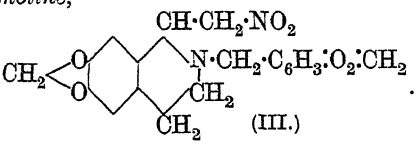
$$CH_2O_2{:}C_6H_3 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot C_6H_3{:}O_2{:}CH_2.$$

—A warm solution of piperonylidene-β-piperonylethylamine (22 g.) (Decker and Becker, *Annalen*, 1913, **395**, 342) in absolute alcohol (500 c.c.) was added as quickly as possible through a long reflux condenser to sodium (35 g.) in a flask immersed in an oil-bath at 140°. When all the sodium had passed into solution, the mixture was cooled and added to water (2000 c.c.). On keeping, colourless crystals separated (15 g.). The base crystallises from light petroleum (b. p. 40—60°) in needles, m. p. 53° (Found: C, 68·0; H, 5·7. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7%). It is readily soluble in alcohol or benzene. The *hydrochloride* is very sparingly soluble in dilute hydrochloric acid and crystallises from much boiling water in flocculent masses of colourless needles. The *nitroso*-derivative, obtained in the usual way, crystallised from alcohol in clusters of minute, colourless needles, m. p. 127—128°. The *dinitro*-derivative, prepared in acetic acid solution, crystallised from alcohol in colourless, diamond-shaped plates, m. p. 134—135°. The N-*formyl* derivative was obtained by refluxing (oil-bath at 180°) a mixture of the base (5 g.) and anhydrous formic acid (25 c.c.) for 2 days. The emulsion obtained on the addition of water resolved into crystals and the solid was purified by trituration with dilute acetic acid (yield, 70%). The substance, which is readily soluble in most organic solvents, crystallised with difficulty from light petroleum in colourless, microscopic prisms, m. p. 89—90° (Found: C, 65·8; H, 5·3. $C_{18}H_{17}O_5N$ requires C, 66·0; H, 5·2%).

6 : 7-*Methylenedioxy*-2-*piperonylmethyl*-3 : 4-*dihydro*isoquinolinium *Picrate and Bromide* (II).—(A). A mixture of formopiperonylmethyl-β-piperonylethylamide (5 g.) and phosphoryl chloride (30 g.) was heated on the steam-bath for 20 minutes and then added to crushed ice. Picric acid (4 g.) was added to the filtered solution and the pasty, yellow mass of the picrate was collected and obtained crystalline by rubbing under alcohol. The derivative crystallised from boiling acetone in microscopic, transparent, yellow rhombs, m. p. 184—185° (yield, 7·2 g.) (Found: C, 53·4; H, 3·4; N, 10·5. $C_{24}H_{18}O_{11}N_4$ requires C, 53·5; H, 3·3; N, 10·4%). (B). Solutions of 6 : 7-methylenedioxy-3 : 4-dihydro*iso*quinoline (3·5 g.) and of

piperonylmethyl bromide (4·4 g.) in benzene (20 c.c. each) were mixed and then heated for 10 minutes on the steam-bath. The yellow crystals (6·8 g.) deposited on cooling separated from alcohol in minute, yellow needles, m. p. 230° (Found: Br, 21·0, 20·4. $C_{18}H_{16}O_4NBr$ requires Br, 20·5%). The salt is sparingly soluble in water, more readily in alcohol, giving pale yellow solutions exhibiting a blue fluorescence. The addition of picric acid to an alcoholic solution gave the picrate, m. p. 184—185°, which was identified by direct comparison with the product obtained in (A).

6 : 7-*Methylenedioxy*-1-*nitromethyl*-2-*piperonylmethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline,



(III.)

—The carbinol from 6 g. of the above-described bromide was extracted with ether, the extract dried with potassium carbonate, and the solvent removed. All these operations should be conducted expeditiously. The residue was dissolved in alcohol (20 c.c.), and nitromethane (1 g.) in alcohol (5 c.c.) introduced. After heating on the steam-bath for a few minutes, the mixture was cooled; the crystals that separated were obtained, after three recrystallisations from alcohol, in short, colourless prisms, m. p. 124—125° (Found: C, 61·5; H, 4·9. $C_{19}H_{18}O_6N_2$ requires C, 61·6; H, 4·9%). The picrate was similarly treated and gave the same derivative with nitromethane; a mixture of the two specimens had m. p. 124—125°.

6 : 7-*Methylenedioxy*-1-*cyano*-2-*piperonylmethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (III with CN instead of $CH_2{\cdot}NO_2$).—When potassium cyanide is added to an aqueous solution of the bromide or of the chloride (derived from the picrate by addition of dilute hydrochloric acid and removal of the picric acid with ether), a curdy, white precipitate is thrown down: this rapidly becomes crystalline. The substance crystallises from alcohol in hexagonal plates, m. p. 151° (Found: C, 67·8; H, 4·8. $C_{19}H_{16}O_4N_2$ requires C, 67·9; H, 4·8%), and has the properties of a pseudo-cyanide. It is insoluble in cold 7% sulphuric acid and, on warming, a yellow solution is obtained and hydrogen cyanide liberated. It dissolves in concentrated hydrochloric acid to a colourless solution and after dilution the unchanged base may be precipitated by ammonia. On heating, however, a yellow solution is obtained.

THE UNIVERSITY, MANCHESTER. [*Received, July 26th,* 1927.]

CCCLI.—*Mercury Derivatives of Acetic Acid.*

By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS.

As is well known, some metallic acetates on being heated break up into acetone and the carbonate of the metal, whilst others, such as those of copper, silver and mercury, give no acetone but pure acetic acid. At about 170—180° mercuric acetate forms a well-defined, intermediate compound which was first described, but not analysed, by F. Stromeyer in 1809 (Göttingen Comment., I, 1808–1811, "De Connubio Hydrargyri cum Acido Acetico." The short paragraph referred to was translated in Gmelin's "Handbook"). The compound has the composition represented by the formula $C_2H_2O_2Hg$ (I) (Found: Hg, 77·2; C, 9·1; H, 0·9. Calc.: Hg, 77·6; C, 9·3; H, 0·7%).

Compounds of the composition $C_2H_2O_2Hg$, and in some cases probably identical with Stromeyer's, have been obtained. Sand and Singer (*Ber.*, 1903, **36**, 3707), by heating dry mercuric acetate with acetic anhydride, obtained a compound to which they gave the constitution $(C_2H_3O_2Hg)_2C<\begin{matrix}CO\\Hg\end{matrix}>O$.

Schrauth and Schoeller (*Ber.*, 1908, **41**, 2090) obtained from mercurimalonic acid a compound to which they gave the formula $CH_2<\begin{matrix}CO\\Hg\end{matrix}>O$ and the name "oxyquecksilber essigsäure anhydrid." The properties of this compound as described by them differ considerably from those of Stromeyer's substance. Biilmann and Witt (*Ber.*, 1909, **42**, 2067) throw doubt on the production of this substance from mercurimalonic acid.

A substituted mercuriacetic acid of a different kind, to which he gave the formula HO·Hg·C(:Hg)·CO_2M, was obtained by K. A. Hoffmann (*Ber.*, 1899, **32**, 875) by heating mercuric oxide with sodium acetate in concentrated alkaline solution.

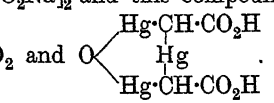
Stromeyer gave no name to his compound, which was probably the first organo-metallic compound to be discovered. We suggest the name *mercuretin*. We have found that mercuretin is formed in other ways than by Stromeyer's method. It gradually separates (Found: Hg, 77·4; C, 8·9; H, 0·9%) when mercuric acetate is boiled with glacial acetic acid, and it is formed completely and at once on addition of acetic anhydride to such a solution (Found: Hg, 77·2; C, 9·2; H, 0·7%). It is known that the reaction is complete when a sample dissolves completely in sodium hydroxide solution without any yellow precipitate of mercuric oxide. Mercurous acetate, which is generally present in mercuretin prepared

by either of these methods or by Stromeyer's, is easily removed by boiling water. The purified mercuretin remains white when treated with ammonia and gives a clear solution with sodium hydroxide. The formation of mercurous acetate is avoided by keeping the temperature as low as possible during the early stages of the reaction, and also when the conversion is carried out in a sealed tube at 190°; no permanent gas is given off in the latter circumstance.

Mercuretin is not soluble in water, but it slowly dissolves with some decomposition in boiling glacial acetic acid. On cooling, crystals are obtained different from the original substance; the composition corresponds with the formula $C_{12}H_{14}O_{12}Hg_5$ (II) (Found: Hg, 74·5; C, 10·4; H, 1·0. Calc.: Hg, 74·6; C, 10·7; H, 1·0%) and the structure may be represented by the formula

$$Hg[C(C_2H_3O_2Hg)_2\cdot CO_2H]_2.$$

When mercuric acetate is heated with sodium acetate a different condensation occurs. The insoluble *substance*, after being washed free from sodium acetate and mercurous acetate, has the composition $C_4H_4O_5Hg_3$ (III) (Found: Hg, 81·2; C, 6·3; H, 0·5. Calc.: Hg, 82·0; C, 6·3; H, 0·5%). The formation and probable structure of this compound can be explained by supposing that the sodium acetate is attacked by the mercuric acetate with the formation of $Hg[CH(CO_2H)\cdot HgC_2H_2O_2Na]_2$ and this compound by the action of water gives $2NaC_2H_3O_2$ and



Mercuric acetate condenses with lead acetate to give a compound completely soluble in sodium hydroxide. The condensation of the two salts may also be brought about by the addition of acetic anhydride to a boiling solution of the two salts in glacial acetic acid. The product remains dissolved in the acetic acid and is obtained by evaporation. Mercuric oxide (2 mols.) also condenses with lead acetate with elimination of water (2 mols.).

Action of Nitric Acid.—Mercuretin dissolves readily and without oxidation in warm nitric acid (*d* 1·4). Crystals are obtained on cooling which, after being washed with nitric acid and dried, have very nearly the composition represented by the mixture

$$(HgNO_3)_3C\cdot CO_2H + (HgNO_3)_2CH\cdot CO_2H \quad (IV)$$

(Found: Hg, 69·9; C, 3·2; H, 0·4; N, 5·3. Calc.: Hg, 70·2; C, 3·2; H, 0·2; N, 4·9%).

If the solution in nitric acid is poured into water a *substance* is precipitated which, after being washed with water and dried, has the composition represented by the formula $Hg_5(NO_3)_2C_4O_4$ (V) (Found: Hg, 80·2; C, 4·1; H, 0·3; N, 2·2. Calc.: Hg, 80·9;

C, 3·9; N, 2·2%). The formation of this compound is readily explained by loss of nitric acid from the substances in solution:

$$\left.\begin{matrix}(NO_3Hg)_3C\cdot CO_2H\\(NO_3Hg)_2CH\cdot CO_2H\end{matrix}\right\} \xrightarrow{-3HNO_3} O_3NHg\cdot\underset{\displaystyle CO\cdot O\cdot Hg}{\overset{\displaystyle Hg\cdot O\cdot CO}{\overset{|}{\underset{|}{C}}}}\cdot Hg\cdot C\cdot HgNO_3$$

Another nitrate was made by boiling a solution of mercuric nitrate in glacial acetic acid. The conversion was complete when a sample dissolved in excess of sodium hydroxide solution without any precipitation of mercuric oxide. The substance crystallised on cooling and had the composition represented by the formula $Hg_5(NO_3)_4C_4H_2O_4$ (VI) (Found: Hg, 73·8; C, 3·4; H, 0·3; N, 3·8. Calc.: Hg, 73·4; C, 3·5; H, 0·15; N, 4·1%). We suggest for it the structure $Hg[C(HgNO_3)_2\cdot CO_2H]_2$.

Action of Ammonia.—Mercuretin is soluble neither in ammonia nor in ammonium acetate, but it dissolves easily in a mixture of the two. On evaporation a nearly white powder is obtained which is not soluble in water but is easily dissolved by an aqueous solution of ammonium acetate and ammonia. After being washed with water and dried, the *substance* had the composition represented by the formula $C_6H_5O_6NHg_5$ (VII) (Found: Hg, 83·1; C, 6·0; H, 0·7; N, 1·3. Calc.: Hg, 84·0; C, 6·0; H, 0·4; N, 1·2%). This compound may be represented as formed by the replacement of two $C_2H_3O_2$ groups in $Hg_5C_{10}H_{10}O_{10}$ by the group NH.

Conclusion.—We think that Stromeyer's compound, which we have called mercuretin, has the molecular formula $C_{10}H_{10}O_{10}Hg_5$. In support of this view, we have the persistence of five mercury atoms in the two nitric acid derivatives (V and VI), in the compound (II), and in the ammonia derivative (VII). The removal of some of the acetic groups by nitric acid and the easy removal of two acetic groups by the action of ammonia indicate that two of the five acetic groups are much less firmly held than the other three. Thus the formula $C_6H_4O_6Hg_3(HgC_2H_3O_2)_2$ is indicated. We suggest for mercuretin accordingly the structure

$$\begin{matrix}Hg\cdot C_2H_3O_2 & & Hg\cdot C_2H_3O_2\\ | & & |\\ CH & — & CH\\ CO\cdot O\cdot Hg & & Hg\cdot O\cdot CO\\ & & |\\ & & CO_2H\end{matrix}$$

and this structure explains readily the simple relationship between mercuretin and substance II, and also its feebly acid nature.

UNIVERSITY MUSEUM, OXFORD. [*Received, September 13th*, 1927.]

CCCLII.—*The Two* o-*Cyanocinnamic Acids.*

By WILLIAM DAVIES and HARRY GORDON POOLE.

ALTHOUGH the two theoretically possible stereoisomeric forms of *o*-cyanocinnamic acid exist, only one form of *o*-carboxycinnamic acid is known, and this is obtained when either of the cyano-acids is hydrolysed (Edwards, J., 1926, 816). It gives the lactone of β-*o*-carboxyphenylhydracrylic acid on heating or on treatment with dehydrating agents, and attempts to prepare the true anhydride failed.

The *o*-cyanocinnamic acid melting at 256° can be obtained in 36% yield by heating the sodium salt of 1-nitroso-2-naphthol with a solvent of suitable boiling point, whereas with the use of sand as diluent (D.R.-P. 116,123) the yield is not more than 5% (Gabriel, *Ber.*, 1916, **49**, 1611). The *o*-cyanocinnamic acid melting at 137° has been prepared after D.R.-P. 411,955 by the action of *p*-toluenesulphonyl chloride on 1-nitroso-2-naphthol in the presence of aqueous alkali. During a large-scale preparation in which the heating during evaporation was very prolonged, an appreciable quantity of acetophenone-*o*-carboxylic acid was produced, possibly owing to the following changes in the $CH{:}CH{\cdot}CO_2H$ group of the carboxycinnamic acid formed by hydrolysis of the cyanocinnamic acid initially produced: $\cdot CH{:}CH{\cdot}CO_2H \longrightarrow \cdot C(OH){:}CH{\cdot}CO_2H \longrightarrow \cdot CO{\cdot}CH_2{\cdot}CO_2H \longrightarrow \cdot CO{\cdot}CH_3$. It is, however, not clear whether the atmosphere or part of the nitrosonaphthol is the oxidising agent, and this abnormal reaction will be further examined.

EXPERIMENTAL.

The Preparation of o-*Cyanocinnamic Acid* (m. p. 256°).—A series of experiments was carried out with *p*-cymene, *o*-nitrotoluene, and nitrobenzene as solvents and the following process was found satisfactory. The dry, finely powdered sodium salt of 1-nitroso-2-naphthol (20 g.) and nitrobenzene (120 c.c.) were heated at 205° for 2 hours. The dark mixture was shaken with a warm aqueous solution of sodium acetate, and the aqueous portion was boiled with animal charcoal and acidified with hydrochloric acid; the buff-coloured precipitate obtained (yield, 6½ g. or 36%) crystallised from nitrobenzene in colourless needles, m. p. 256° (decomp.).

This *o*-cyanocinnamic acid sublimes almost unchanged at 225°/1 mm. It is not attacked by cold concentrated sulphuric acid exposed to air, and no trace of an acid amide is formed on prolonged standing. Hydrolysis with concentrated aqueous alkaline solutions gives a large quantity of tar and only a small amount of

o-carboxycinnamic acid (m. p. 184°). The identity of this carboxycinnamic acid with that from *o*-cyanocinnamic acid (m. p. 137°) was proved by the method of mixed melting points.

Preparation of o-*Cyano*allo*cinnamic Acid* (m. p. 137°) *after* D.R.-P. 411,955.—To a solution of 1-nitroso-2-naphthol (from 50 g. of β-naphthol *) in aqueous sodium hydroxide [45 g. (3¼ mols.) in 1 l.] at 75°, *p*-toluenesulphonyl chloride (65 g.) was added all at once. The temperature was then rapidly raised to 100° and maintained for 15 minutes; a vigorous reaction began at 85°. Some tar was filtered off when cold, and after acidification a large, orange-yellow precipitate settled out. When this was crystallised from hot water, 15 g. of cyanocinnamic acid (m. p. 137°) were obtained, and subsequently 6 g. of a yellow, granular material.

Acetophenone-o-carboxylic Acid.—In a preliminary experiment (1-nitroso-2-naphthol from 200 g. of β-naphthol; 10 l. of water; 3¼ mols. of sodium hydroxide; 320 g. of *p*-toluenesulphonyl chloride) the procedure was as described above. After the 15 minutes' heating at 100°, the mixture was rapidly cooled to 40° with ice. A large amount of a green substance like the sodium salt of nitrosonaphthol was left. The filtrate from this was evaporated to 4½ litres, and the green substance (assumed to be the sodium salt of nitrosonaphthol) then added together with the requisite amounts of sodium hydroxide and toluenesulphonyl chloride. The mixture was kept at 100° for 15 minutes, and on cooling, a green precipitate was again formed. The filtrate when acidified with hydrochloric acid gave much tar, and after the removal of this the solution was again made alkaline with sodium hydroxide solution; a dark substance slowly separated from the deep red solution. This solution was concentrated and acidified with hydrochloric acid, whereby, instead of *o*-carboxycinnamic acid, a deep red oil was produced. This was extracted with ether, the ether removed, and the pasty residue crystallised from water, 20 g. of crude crystalline acetophenone-*o*-carboxylic acid being obtained. This crystallised from benzene in colourless prisms, which melted at 114—115° and had a sweet taste (Found: equiv., 165·4; *M*, by Rast's method, 163, 171; H, 5·2. Calc. for $C_9H_8O_3$: equiv. and *M*, 164; H, 4·9%) (compare Gabriel and Michael, *Ber.*, 1877, **10**, 1554. Rule and Smith, J., 1926, 556, record m. p. 112°). The *oxime* crystallised from alcohol in colourless needles, m. p. 156—157°, and the p-*nitrophenylhydrazone* in minute, yellow, felted needles, m. p. 211°. The *phenylhydrazone*

* β-Naphthol is nitrosated in about 85% yield after Lagodzinski and Hardine (*Ber.*, 1894, **27**, 3075), and is most conveniently used moist. The nitrosonaphthol is difficult to dry completely, and the sodium salt when dry is very sternutatory.

is too soluble in water to be a convenient derivative for identification. The acid was smoothly converted into phthalic acid by oxidation with permanganate solution.

Properties and Derivatives of o-*Cyano*allo*cinnamic Acid.*—On being heated slightly above its melting point under 1 mm. pressure, this acid distils with some decomposition. The oily distillate, which has the odour of styrene, contains the isomeric *o*-cyanocinnamic acid, m. p. 256°. The *allo*-acid is easily hydrolysed to the corresponding dicarboxylic acid (m. p. 184°).

o-*Cyano*allo*cinnamyl chloride* is best prepared by heating the corresponding acid with a slight excess of thionyl chloride for 1 hour; the excess of thionyl chloride is then removed in a vacuum. The residual acid chloride crystallises from petroleum (b. p. 120°) in colourless needles, 2 cm. long (Found: Cl, 18·4. $C_{10}H_6ONCl$ requires Cl, 18·5%). It melts at 50°, and is extremely soluble in benzene, ether, or dichloroethylene, and sparingly soluble in cold light petroleum. Ethyl and methyl alcohol convert it into the ethyl and methyl esters of the lactone of β-*o*-carboxyphenylhydracrylic acid (Roth, *Ber.*, 1914, **47**, 1598), m. p. 76° and 62°, respectively.

The authors wish to thank Mr. F. C. Woods, M.Sc., for assistance in preparing the *o*-cyanocinnamic acid of m. p. 256°.

MELBOURNE UNIVERSITY, AUSTRALIA. [*Received, April 20th*, 1927.]

CCCLIII.—*Beryllium Dialkyls.*

By HENRY GILMAN and F. SCHULZE.

IN continuation of studies on organoberyllium halides (Gilman, *J. Amer. Chem. Soc.*, 1925, **45**, 2693; see also Durand, *Compt. rend.*, 1926, **182**, 1162) it was necessary to prepare some beryllium dialkyls for comparative purposes, inasmuch as the two classes of compounds appear to be interconvertible.

Cahours (*Ann. Chim. Phys.*, 1860, **58**, 22) claimed to have prepared beryllium diethyl by heating the metal with ethyl iodide in a sealed tube. Later (*Compt. rend.*, 1873, **76**, 1383. Cahours's work on beryllium dialkyls has been discussed by Frankland, J., 1861, **13**, 181, 194) he reported the preparation of beryllium diethyl and beryllium dipropyl by heating the metal with the corresponding mercury dialkyls in a sealed tube at 130°. It is highly probable that Cahours's work on beryllium diethyl is incorrect. His beryllium diethyl was distilled in an atmosphere of carbon dioxide and boiled

at 185—188°. We have found that beryllium diethyl not only reacts with carbon dioxide, but also boils at a much higher temperature range (with decomposition) than that reported by Cahours. Furthermore, we had no success in the preparation of beryllium diethyl and beryllium di-*n*-butyl from the mercury dialkyls as recommended by Cahours. Incidentally, Cahours incorrectly described magnesium diethyl as a liquid, inasmuch as it is a solid (Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, 2328).

Lavroff (*J. Russ. Phys. Chem. Soc.*, 1884, **16**, 93; *Bull. Soc. chim.*, 1884, **41**, 548) very briefly mentioned the preparation of beryllium dimethyl by the action of beryllium on mercury dimethyl in a sealed tube at 130°. We have found no further mention of his work. Despite the very meagre detail in his preliminary communication, it is quite probable that he did have beryllium dimethyl.

Krause and Wendt (*Ber.*, 1923, **56**, 467, footnote 2) state that beryllium dialkyls may be prepared by the reaction between beryllium chloride and an excess of Grignard reagent.

Experimental.

Several unsuccessful attempts were made to prepare beryllium diethyl and beryllium di-*n*-butyl from finely crushed beryllium and equivalent quantities of the corresponding mercury dialkyls. No evidence of reaction was obtained when the mixtures were kept in sealed tubes for 3 weeks at room temperature; when they were heated for 3 weeks at 90°, some free mercury was formed, and heating for 15 hours at 130°, 175°, 200°, and 225° apparently induced only decomposition of the mercury dialkyls; in no case was there evidence of the formation of beryllium dialkyls.

Beryllium diphenyl and beryllium di-*p*-tolyl may be readily prepared by heating beryllium with equivalent quantities of mercury diphenyl and mercury di-*p*-tolyl and a trace of mercuric chloride in sealed tubes at 225° for 6 hours.

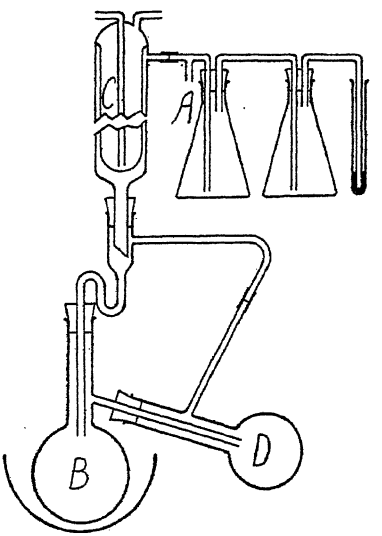
In the experiments with mercury dialkyls, no mercuric chloride was added. Other studies (Gilman and Schulze, *loc. cit.*) have shown that mercuric chloride is an almost indispensable catalyst in the preparation of some metallic dialkyls, like magnesium diethyl. No attempt was made to prepare beryllium dimethyl from beryllium and mercury dimethyl. It is quite reasonable to assume that traces of some mercuric halide were contained in the materials used by Lavroff. The beryllium used in the present studies was obtained from the Beryllium Corporation of America and contained more than 99·5% of beryllium.

It is possible to prepare beryllium dialkyls by heating beryllium with the appropriate alkyl halides, an alkylberyllium halide being

an intermediate product. Here, again, mercuric chloride is a very helpful catalyst.

However, it appears that the most convenient method for the preparation of beryllium dialkyls is the reaction between anhydrous beryllium chloride and the appropriate Grignard reagent. We have prepared beryllium dimethyl, diethyl, and di-*n*-butyl by this method.

Preparation of Beryllium Dialkyls.—Because of the highly hygroscopic nature of anhydrous beryllium chloride and the ready decomposability of beryllium alkyls and the Grignard reagent by air, all operations were carried out in pure dry hydrogen or nitrogen, admitted through the tube *A*. Anhydrous beryllium chloride (8 g.; 0·1 g.-mol.) is dissolved in 50 c.c. of anhydrous ether, cooled by running water. The filtered oily solution, which may be either colourless or pale yellow and separates into a lower layer of beryllium chloride etherate and an upper layer consisting largely of ether, falls directly into 75 c.c. of 4*M*-magnesium methyl iodide (0·3 g.-mol.) contained in a 250 c.c. flask, *B*, the Grignard solution being gently shaken during addition. There is little heat of reaction if the beryllium chloride solution is pure and anhydrous. The formation of white clouds on the surface of the reaction mixture is indicative of the presence of air or oxygen.



The excess of ether is removed by stopping the circulation of water in the condenser, *C*, until the oil-bath attains a temperature of 150°. The water is then turned on slowly in order to prevent a too sudden contraction (due to the condensation of ether) that might draw air into the condenser and receiving flask. Distillation is continued at 150—200° for 6 to 15 hours, so long as an ethereal solution of beryllium dimethyl collects in the receiving flask, *D*. Heat radiating from the oil-bath is sufficient to keep the temperature of the receiver above the boiling point of ether and thereby prevent the condensation of more ether than is necessary to hold the beryllium dimethyl in solution. The distillation may be continued overnight, as it requires no attention. Should the ether be driven out

completely from the distilling flask, *B*, so that no more ether vapour circulates, it is necessary merely to heat the receiver gently to return the ether to flask *B*. Such heating should be moderate, otherwise some of the beryllium dimethyl will be driven back into *B* and so extend the time of recovery of the compound.

The ethereal solution of beryllium dimethyl obtained in this manner is clear and colourless (when care has been taken to exclude air), and it may be used directly in a study of the reactions of the compound. When not in use, it is kept preferably in sealed glass containers. Pure, ether-free beryllium dimethyl is obtained by heating the distillate. At about 100—125°, most of the ether is expelled and the whole solution suddenly turns to a mass of white needles containing some ether, which may be removed by heating to 200°. At 200° (external temperature), the compound commences to sublime rapidly, and part of it solidifies in the capillary when a constricted test-tube is used for the collection of ether-free samples. However, the capillary can be kept open prior to sealing by applying a small luminous flame. A repetition of this process of distillation in a sealed U-tube arrangement originally filled with ether vapour makes it possible to obtain material free from oxide or methoxide by alternately heating and cooling each part of the U-tube. The samples used for analysis were prepared in this manner.

3·5 G. (90% yield) of beryllium dimethyl were obtained from 0·1 g.-mol. of beryllium chloride; with 0·3 g.-mol., the yield was 84·7%.

Beryllium diethyl and di-*n*-butyl were prepared in essentially the same way as beryllium dimethyl. However, it is possible to distil beryllium diethyl and di-*n*-butyl directly in a vacuum. Because of the higher vapour pressure of beryllium di-*n*-butyl, it would probably be more advantageous to use a vacuum distillation rather than the ether distillation or ether sublimation process used for the dimethyl compound.

Analysis of Beryllium Dimethyl.—After being weighed, one of the sealed tubes, containing beryllium dimethyl prepared by distillation at 200°, was broken in a vessel filled with dry ether, and the volume of methane liberated on the addition of water and then dilute hydrochloric acid was measured in a special eudiometer containing concentrated sulphuric acid. An aliquot portion of the evolved gas, when exploded with a measured volume of oxygen, was shown to consist of pure methane.

The beryllium was analysed as beryllium oxide after careful removal of the glass, which was weighed to determine the weight of beryllium dimethyl originally present in the sealed container [0·1501 g. of beryllium dimethyl gave 173·2 c.c. (corr.) of methane

and 23·33% of beryllium. Calc.: 171·4 c.c. and 23·25%. 0·1771 G. gave 200·7 c.c. of methane. Calc.: 202·2 c.c.].

Properties of Beryllium Dialkyls.—Beryllium dimethyl crystallises from hot concentrated ethereal solution in snow-white needles (see Preparation). It is also deposited in the same form when it sublimes, without melting, at about 200°. The method of preparation is based on its high volatility in ether, and these ethereal solutions fume strongly when exposed to the atmosphere. When suddenly overheated, it undergoes partial decomposition, leaving a brown or grey mirror.

Beryllium diethyl is a colourless liquid, b. p. 93—95°/4 mm. and 110°/15 mm. It distils between 180° and 240° at atmospheric pressure with considerable decomposition. The compound is only distilled with difficulty because of its pronounced tendency to become superheated and then break suddenly into foam. This may be due to the decomposition of an etherate. A part of the purest material solidified, in a carbon dioxide–ether freezing mixture, to white crystals which on warming melted at −13° to −11°.

Beryllium di-*n*-butyl is a clear, colourless liquid having a mercaptan-like odour. The boiling point, 170°/25 mm., was determined with a rather small quantity of material and so may not be taken with too much credence.

Both beryllium dimethyl and diethyl are spontaneously inflammable in the air, and especially so in a humid atmosphere. Even concentrated ethereal solutions are inflammable spontaneously in the presence of moist air. The compounds burn with luminous flames, evolving dense white fumes of beryllium oxide. Their very high sensitivity to oxygen made it difficult, at first, to purify the hydrogen or nitrogen to such an extent that it would not give a white cloud of beryllium oxide when passed over the ethereal solutions of the dialkyls. For this reason, a magnesium phenyl bromide solution was inserted in the drying and purifying train in order to remove a residuum of oxygen. Beryllium di-*n*-butyl is not spontaneously inflammable when exposed to the air. But it does oxidise rapidly, when so exposed, with the evolution of heat. Very probably, beryllium butyloxide is a product of such oxidation, inasmuch as the odour of *n*-butyl alcohol becomes quite pronounced after a short air exposure.

The reaction of the dialkyls with water is violent, and in the presence of small amounts of water the materials frequently inflame. Methane and ethane are evolved when the corresponding dialkyls are decomposed by water.

Beryllium dimethyl in the solid state inflames when treated with carbon dioxide. With an ethereal solution, however, the reaction

is quite mild and acetic acid is formed. An ethereal solution of beryllium diethyl reacts with carbon dioxide to give triethylcarbinol.

Phenylcarbimide in ethereal solution reacts with extreme violence with the three dialkyls studied. In each case, a white solid separated at first, and then dissolved in the excess of beryllium dialkyl. The expected anilides were obtained, the valeranilide as an oil. This anilide is known to crystallise with difficulty, so that its identity has not been confirmed, as was done with the other two anilides, by a mixed-melting point determination with an authentic specimen. Aceto-α-naphthalide was obtained from beryllium dimethyl and α-naphthylcarbimide.

The three dialkyls give an immediate positive colour reaction with Michler's ketone according to the test described by Gilman and Schulze (*J. Amer. Chem. Soc.*, 1925, **47**, 2002) for RMgX and some other organometallic compounds. The blue instead of green colour given by beryllium di-*n*-butyl indicates that this dialkyl probably reduced the ketone to Michler's hydrol (*loc. cit.*).

Beryllium dimethyl with benzophenone gave diphenylmethylcarbinol, which was identified as αα-diphenylethylene. Beryllium diethyl, on the other hand, reduced benzophenone to benzhydrol. In the latter reaction, a bright orange-red colour was present transitorily at the junction of the two liquids. This may be indicative of the intermediate formation of a free radical.

Beryllium dimethyl with benzoyl chloride gave phenyldimethylcarbinol, and this was identified by the formation of *iso*propenylbenzene when the carbinol was distilled. The reaction product was probably free from acetophenone as indicated by a test with semicarbazide.

The beryllium dialkyls appear to have high solvent characteristics, for all the intermediate reaction products dissolved in an excess of the dialkyl. Equally striking is the fact that beryllium diethyl dissolved the beryllium oxide and ethoxide formed by partial decomposition of the dialkyl, as well as the brown or grey mirror formed by the high-temperature decomposition of the dialkyl.

Beryllium dimethyl and diethyl react vigorously with iodine. When 1·343 g. of beryllium dimethyl were treated with 1 equiv. (4·353 g.) of iodine, the solution still contained some dialkyl, as was evidenced by the fuming on air exposure and by a slight positive test (Gilman and Schulze, *loc. cit.*). After standing for several days in a cork-stoppered flask, the solution no longer fumed and gave a negative test. Very probably beryllium methyl iodide was formed as a result of the iodine reaction, because the solution gave acetanilide on treatment with phenylcarbimide, and when heated it fumed and gave a positive test. These are among the criteria

included for the characterisation of beryllium alkyl halides (Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, Nov.).

Beryllium diethyl reacts with an excess of an ethereal solution of beryllium chloride to give a solution with the characteristics of beryllium ethyl chloride. In view of these latter experiments, the following equilibrium is probable under certain conditions:

$$BeR_2 + BeX_2 \rightleftharpoons 2RBeX.$$

In general, the beryllium alkyl halides are less active than the beryllium dialkyls, and the beryllium dialkyls are at least equal in activity to the Grignard reagents.

IOWA STATE COLLEGE,
AMES, IOWA, U.S.A. [*Received, August 2nd*, 1927.]

CCCLIV.—*The Thermal Dissociation of Strontium Carbonate.*

By EDWARD OSWALD JONES and MAURICE LUND BECKER.

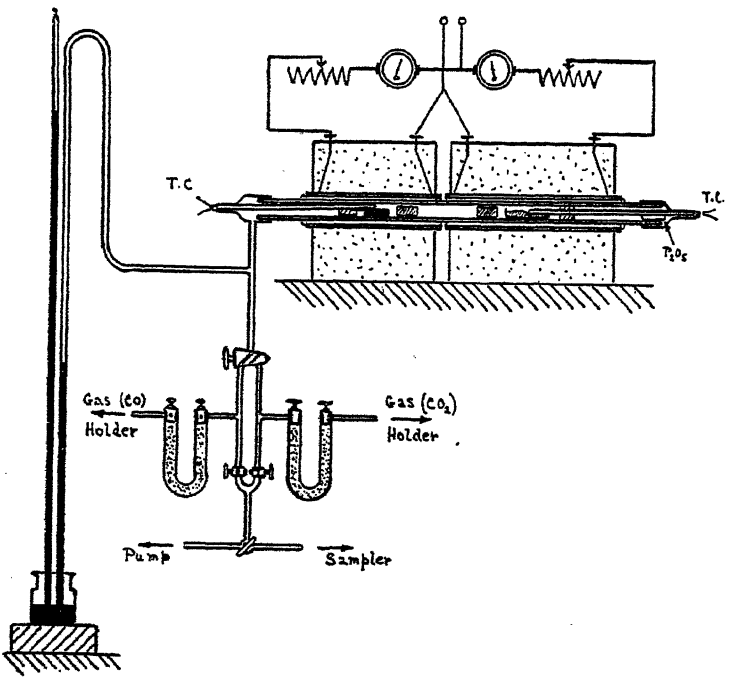
DURING their work on the effect of temperature and pressure on the progress and equilibrium of certain reactions, the authors were faced with the problem of devising a suitable means by which the composition of a gas phase consisting of carbon monoxide and dioxide could be readily determined at any instant. It occurred to one of them (E. O. J.) that a suitable method of attack would be to fix the partial pressure of the carbon dioxide by maintaining the gas phase in contact with a carbonate heated to a known temperature. The pressure of this gas would be the dissociation tension of the carbonate for that particular temperature, and by subtraction from the total pressure of the system the partial pressure of the monoxide could be found.

The alkaline-earth carbonates naturally suggested themselves as being suitable materials for the purpose, and a study of the literature led to the selection of strontium carbonate. The only work on the dissociation tension of this carbonate at different temperatures to which reference could be found was that of Pott (Diss., Freiburg, 1905; see also Mellor, "Treatise on Inorganic and Theoretical Chemistry," III, 655). Two other workers, Brill (*Z. anorg. Chem.*, 1905, **45**, 275) and Hedvall (*ibid.*, 1916, **98**, 47), record determinations of the temperature at which the tension attains 1 atm. Unfortunately, their work is not in good agreement with that of Pott, and it was further noted that Pott's curve is of quite a different shape from those given for calcium and barium carbonates, and actually cuts the first of these two curves. It

was thought advisable, therefore, to make a series of determinations of the dissociation tension of strontium carbonate at different temperatures in the same apparatus and under the same experimental conditions as those in which it was proposed to use this material for carbon dioxide-pressure control.

During the course of the investigations, two distinct types of apparatus were employed. These are diagrammatically represented in Figs. 1 and 2. The first was designed for use where it was neces-

FIG. 1.



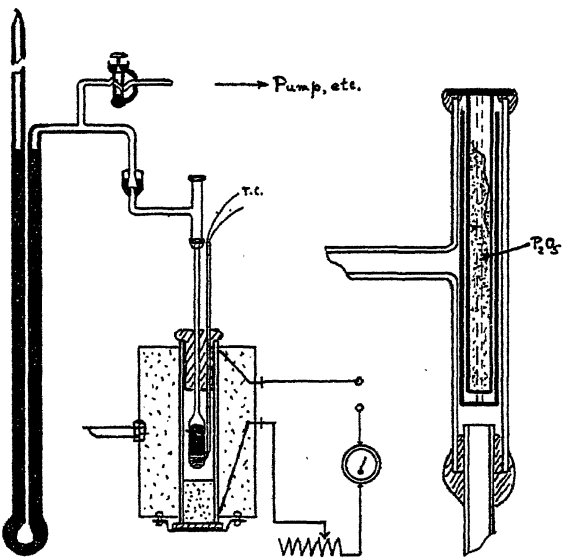
Apparatus No. 1. (Diagrammatic.)

sary to keep the carbonate separate from the other reactants with the gas phase, and where independent temperature control, both of the reactants and of the dissociating carbonate, was desirable. The second, which is simpler, was utilised when the above-mentioned limitations did not apply.

Apparatus 1 consists essentially of a long porcelain tube (800 mm. × 18 mm. internal diameter) heated by two independently controlled electric resistance furnaces. The ends of the tube were closed by glass caps hermetically sealed to the heating tube by white wax. Each of these caps had a small-bore extension to

take the thermocouple sheath, and one of them was also provided with a side tube which gave connexion to the manometer, evacuating pump, gas holders, etc. The Vitreosil thermocouple sheaths were sealed into the extension tubes of the caps by means of white wax, and it was also found advisable to close the open ends of these sheaths with wax, since, after being maintained at high temperatures for a considerable time, they developed slight porosity at the heated end, due to devitrification. Heat-insulating plugs, made of kieselguhr bonded with a small proportion of sodium silicate, were placed in the furnace tube to lessen heat radiation

FIG. 2.



Apparatus No. 2. (Diagrammatic.)

and to provide zones of uniform temperature. A boat containing phosphorus pentoxide, placed at one end of the tube, served to absorb all the water vapour.

Apparatus 2 is essentially a small, transparent silica bulb of about 10 c.c. capacity fused to a silica tube (30 mm. × 5 mm.), the other end of which is sealed by white wax into a glass T-piece. This serves to accommodate a small container for phosphorus pentoxide and to give connexion to the manometer, etc. A small resistance furnace, which may be raised or lowered, serves to heat the bulb to the required temperature, which is measured by a thermocouple in contact with the bulb wall.

This second form of apparatus is more suitable for measuring

dissociation tension, since equilibrium conditions are attained much more rapidly as a result of its small volume and its relatively larger carbonate content. Nevertheless, since it was necessary to use the first form of apparatus for some of the investigations, it was considered desirable to study the thermal dissociation of the carbonate in both forms of apparatus as a matter of precaution and for the sake of calibration. The results obtained were found to agree within the limits of experimental error, and this concordance is considered good presumptive evidence of the correctness of the values obtained.

The experimental details were essentially the same for each type of apparatus. A sufficient quantity of pure strontium carbonate (about 1 g. in the case of the bulb, and 4—5 g. in a porcelain boat in the case of the tube) having been introduced, the apparatus was hermetically sealed and then evacuated by means of a " Cenco Hyvac " pump. The temperature was now raised gradually to about 600°, during which time the evolved gases (largely water vapour) were removed at frequent intervals by pumping. When no more gas appeared to be given off, the temperature was raised to 1000° and maintained at this value for about 12 hours. During this time the pressure increased gradually, due probably to further expulsion of occluded gas and to a slow reaction between the carbonate and the silica walls of the bulb where contact occurs, whereby carbon dioxide was liberated. The apparatus was then evacuated rapidly, the tap to the pump closed, and the pressure allowed to attain a steady value. This was lower than the initial one obtained and the process was repeated as often as was necessary to obtain two consecutive equal values for the gas pressure. This procedure ensured (*a*) removal of all occluded gas, and (*b*) the presence of more strontium oxide than that equivalent to the carbon dioxide liberated by the slow reaction already mentioned. That this is so is shown by the fact that, on allowing the furnace to cool to 600°, the resulting vacuum was of a higher order than could be obtained by the pump alone, *i.e.*, less than 0·05 mm.

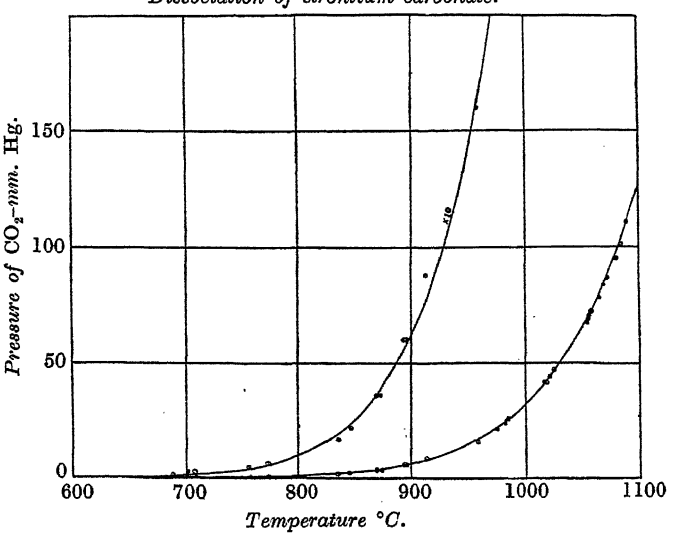
The apparatus was now ready for use. The strontium carbonate was slowly heated, and pressure and temperature readings were taken. In the case of the bulb apparatus, the rate of heating was sufficiently slow to ensure that the pressure corresponding to a given temperature was the equilibrium pressure until about 900° had been reached. Beyond this temperature, the furnace was allowed to reach a steady state before readings were taken. In the case of the tube furnace, the method of allowing the furnace to reach a steady temperature was practised from the beginning, as the gas evolution involved was so much larger.

The temperature was measured by means of carefully calibrated thermocouples and is considered accurate to within $\pm 3°$; pressures less than 10 mm. were read by means of a cathetometer to within $\pm 0{\cdot}05$ mm.; higher pressures were read directly on a metre scale fixed alongside the manometer. This gave readings to within $\pm 0{\cdot}5$ mm., which is as close as is justified by the accuracy of the temperature measurements.

Values of the dissociation tension for given temperatures were obtained on both ascending and descending temperature scales and

FIG. 3.

Dissociation of strontium carbonate.



further checked by haphazard alteration of the temperature; the concordance was good. In view of this agreement, there is no need to quote more than one set of results. Those obtained by one of the authors (M. L. B.) are recorded in Table I (in mm. Hg) and shown graphically in Fig. 3.

TABLE I.

Temp.	p, obs.	p, calc.	Temp.	p, obs.	p, calc.
689°	0·1	0·07	975°	21	21·5
708	0·3	0·12	984	25	24·5
756	0·5	0·35	1020	42	42
775	0·6	0·55	1027	47·5	47
835	1·7	1·85	1059	72·5	72
846	2·2	2·3	1070	84	84
869	3·6	3·5	1081	95	97
896	6·0	5·8	1090	111	110
913	8·8	7·8	1103	123	130
958	16·0	16·3			

The dissociation tensions of calcium and barium carbonates determined by various workers have been found to fit closely to curves of the form

$$\log p_1 - \log p_2 = -K(1/T_1 - 1/T_2)$$

where p_1 and p_2 are the pressures (mm. Hg), T_1 and T_2 the absolute temperatures, and K is a constant. It was of interest, therefore, to see whether the dissociation of strontium carbonate could be similarly expressed. If the value of the dissociation tension at 928° be taken as 10 mm. and K as $1{\cdot}05 \times 10^4$, then the values of the carbon dioxide pressure for other temperatures can be calculated. The resulting graph, as will be seen, agrees very satisfactorily with the observed values over the entire range investigated. Table II gives calculated values of the dissociation pressure for temperature increments of 50°.

TABLE II.

Temp.	p, mm.	Temp.	p, mm.	Temp.	p, mm.
650°	0·023	900°	6·19	1150°	231
700	0·090	950	14·36	1200	411
750	0·30	1000	31·22	1258	760
800	0·91	1050	63·98	1300	1167
850	2·47	1100	124·5		

It has already been pointed out that good concordance existed between the results obtained in the different apparatus, and further confirmation, particularly of the lower values as corrected to the calculated curve, is given by later work on the C–CO–CO_2 equilibrium where the carbon dioxide pressure is controlled by means of strontium carbonate. The values of the equilibrium constant thus determined for this system at different temperatures lie closely on Tigerschiöld's curve (*Jernkontoret's Annaler*, 1923, 67; see also Johansson and von Seth, *J. Iron and Steel Inst.*, 1926, **114**, 313) which correlates satisfactorily the work of Boudouard (*Ann. Chim. Phys.*, 1901, **24**, 5), Schenck (*Ber.*, 1905, **38**, 2139), and Rhead and Wheeler (J., 1910, **97**, 2178) on this equilibrium. This agreement justifies the acceptance of the results, and, in particular, the validity of the formula for calculating the dissociation tension in the lower temperature range.

The authors' value for the temperature at which the dissociation pressure is equal to 1 atm. is approximately 100° higher than those reported by Brill (*loc. cit.*) and Hedvall (*loc. cit.*). Although the authors' result has been obtained by extrapolation of the curve, whereas the others have experimental basis, it is regarded as more accurate for the following reasons. (*a*) Brill noted the temperature at which loss of weight just occurred from calcium carbonate in a

carbon dioxide atmosphere of approximately 760 mm. pressure, and obtained a value 75—100° lower than those recorded by other workers who measured the actual dissociation tension. This discrepancy for calcium carbonate is of the same order as the difference between Brill's result for strontium carbonate and the one put forward in this paper.

(*b*) Hedvall, who used the thermal arrest in the heating curve for fixing the dissociation temperature, gives 1141° as the temperature at which carbon dioxide evolution commences. It is of interest, however, that he quotes 1255° (only 3° different from the value put forward by the authors) as the temperature at which carbon dioxide evolution becomes rapid, and further states that a small quantity of strontium carbonate was not completely decomposed on being heated for 5 minutes at temperatures between 1141° and 1255°.

The authors' curve lies wholly between the accepted curves for calcium carbonate (Johnston, *Z. physikal. Chem.*, 1908, **62**, 330; *J. Amer. Chem. Soc.*, 1910, **32**, 938) and barium carbonate (Finkelstein, *Ber.*, 1906, **39**, 1585), thus differing from that of Pott. It is suggested that the higher values obtained by Pott in the lower temperature range are due to the absence of sufficient oxide phase to absorb the excess carbon dioxide liberated by some such slow carbonate–silica reaction as was noticed by the authors in their work. At higher temperatures, where the extent of dissociation involves the production of larger quantities of strontium oxide, this source of error tends to disappear, and it is of interest to note that Pott's results for 1256° and 1263° (744 mm. and 785 mm., respectively) would lie satisfactorily on the extrapolated portion of the authors' curve.

In view of the fact that Finkelstein (*loc. cit.*) obtained evidence of the formation of a basic barium carbonate ($BaO,BaCO_3$), the authors sought for indications of a similar basic strontium carbonate. When the dissociation tensions at 1000° and 1100° were being measured, a known volume (approximately one-sixth of the available carbon dioxide) was drawn off and the system allowed to return to equilibrium. The resulting pressure was the same as in the initial determination. This process was repeated until six withdrawals had been made. In every case, except the last, the pressure returned to the recorded equilibrium value, whilst on the last occasion the pressure only rose a few mm., showing that the solid phase was now wholly the oxide. This series of experiments shows that over the range 15—85 mols. % of strontium oxide the solid phase does not change in character, and therefore affords no evidence for the existence of a basic carbonate under these conditions.

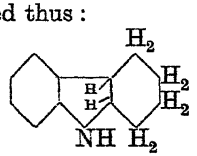
The work here described was carried out in the Metallurgical Department, Manchester University, and the authors desire to express their thanks to Prof. F. C. Thompson, D.Met., for the facilities provided and also for his interest and helpful criticisms and suggestions during the course of the work. Acknowledgment is also due to the Department of Scientific and Industrial Research and to the British Cast Iron Research Association for their financial grants and for their permission to publish the results.

THE UNIVERSITY, MANCHESTER. [*Received, September 7th*, 1927.]

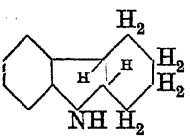
CCCLV.—*A New Stereoisomeride* (trans-) *of Hexahydrocarbazole.*

By JOHN GURNEY, WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

DURING the course of experiments on octahydroacridine, Perkin and Sedgwick (J., 1924, **125**, 2437) showed that this substance exists in two stereoisomeric, externally compensated modifications, namely (A), m. p. 82°, and (B), m. p. 72°, and these they subsequently resolved (J., 1926, 438) each into its optically active components. In the earlier paper, it was pointed out that hexahydrocarbazole also should exist in two analogous stereoisomeric forms, which may be represented thus :



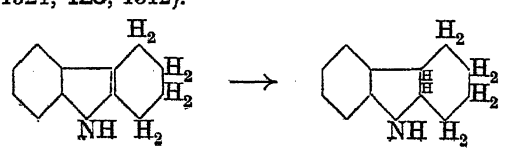
cis.



trans.

and it was proposed to investigate this point.

Hitherto only one form of hexahydrocarbazole (m. p. 99°) has been described. Although this substance has been obtained by the reduction of carbazole under various conditions (Graebe and Glaser, *Ber.*, 1872, **5**, 14; *Annalen*, 1872, **163**, 352; Schmidt and Sigwart, *Ber.*, 1912, **45**, 1784), the only practicable method for preparing relatively large quantities is by the hydrogenation of the double bond in tetrahydrocarbazole (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 70; Carrasco, *Gazzetta*, 1908, **38**, ii, 303; Perkin and Plant, J., 1924, **125**, 1512).



By reducing a large quantity (900 g.) of tetrahydrocarbazole with tin and hydrochloric acid we have now succeeded in isolating a small amount (about 12 g.) of the second isomeride of hexahydrocarbazole, and we find that this melts at 127°. Its identity has been confirmed by making the *picrate* and *acetyl* and *benzoyl* derivatives, and comparing these with the corresponding derivatives of the ordinary form. Both modifications of hexahydrocarbazole have been shown to be unimolecular, they distil unchanged at the ordinary pressure at approximately the same temperature, and are both exceptionally volatile in steam.

The existence of two stereoisomerides of hexahydrocarbazole can be predicted from the Sachse–Mohr theory of multiplanar rings and forms an interesting addition to the cases of this kind which have been already described. This type of stereoisomerism has been recently well established by several investigators in the decahydronaphthalene series, and in a few other dicyclic systems composed of two six-membered rings (see, *e.g.*, Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 91; Perkin and Sedgwick, *loc. cit.*; Helfer, *Helv. Chim. Acta*, 1926, **9**, 814; Hückel and Stepf, *Annalen*, 1927, **453**, 163). In all these cases, both the *cis*- and the *trans*-modifications can be regarded as strainless. The points of particular interest involved in the case of hexahydrocarbazole are (1) that the stereoisomerism is a feature of a dicyclic system composed of one six-membered carbon ring and one five-membered ring containing nitrogen, and (2) that both isomerides are produced together from the same substance in the same reaction. It is quite apparent that in this system there is far more strain in the *trans*-structure than in the *cis*-, a fact which is easily demonstrated with the aid of models. It is to be expected, therefore, that in the formation of such a dicyclic system by the hydrogenation of the double bond common to both rings the *cis*-modification will be produced to a much greater extent than the *trans*-modification, and this is exactly what is observed in the case of the hexahydrocarbazoles. There can be little doubt that the modification, m. p. 99°, which constitutes almost the entire product, is the *cis*-, and that the new substance, present to the extent of 1—2%, is the corresponding *trans*-form.

Hückel and Friedrich (*Annalen*, 1926, **451**, 132) have isolated the *cis*- and *trans*-modifications of the hexahydro-β-hydrindones and the three hexahydro-β-hydrindols, which contain dicyclic carbon systems composed of one six-membered and one five-membered ring, but each of these isomerides was obtained synthetically by independent reactions starting with the *cis*- and *trans*-forms of ethyl *cyclo*hexane-1 : 2-diacetate, respectively. These authors also point

out that the *trans*-configuration in these systems is marked by considerable strain. The anhydrides of *cis*- and *trans-cyclo*hexane-1 : 2-dicarboxylic acid (Windaus and Hückel, *Nachr. Ges. Wiss. Gottingen, Math.-physik. Klasse*, 1920, **11**, ii, 181) also may be considered as examples of the type of dicyclic system which is being discussed in this communication. We are engaged in the attempt to resolve the *cis*- and *trans*-modifications of hexahydrocarbazole into their active components.

EXPERIMENTAL.

A mixture of tetrahydrocarbazole (900 g.), alcohol (1800 c.c.), concentrated hydrochloric acid (1800 c.c.), and granulated tin (1800 g.) (compare Borsche, Witte, and Bothe, *loc. cit.*) was heated on the steam-bath for 5 hours, as much alcohol as possible was then distilled off and the residue was poured into beakers and allowed to cool. The product partly solidified to a crystalline mass, which was pulverised, and the whole was then made strongly alkaline by the addition of concentrated aqueous sodium hydroxide. The solid was collected on asbestos, pressed as dry as possible, and then extracted in portions twice with ether. The solid remaining was ground to a paste with more aqueous sodium hydroxide, collected, and again extracted twice with ether. After removal of the ether by distillation, the crude reduction product was crystallised from alcohol and a large quantity of *cis*-hexahydrocarbazole (m. p. 99°) was obtained. By concentrating the mother-liquor three times, further quantities of *cis*-hexahydrocarbazole were obtained. The alcohol was then removed as completely as possible on the steam-bath from the remaining mother-liquor, the residual product dissolved in 60% sulphuric acid, and the solution poured into much water. The small quantity (38 g.) of unchanged tetrahydrocarbazole thus precipitated was removed, and the aqueous solution made alkaline by the addition of concentrated ammonia, which precipitated the crude mixture of the hexahydrocarbazoles as a colourless solid. The product was made into a paste with water, added to an excess of dilute aqueous sodium hydroxide, and shaken with an equal weight (130 g.) of benzoyl chloride. After a few hours, the solid product was collected and crystallised from alcohol; a considerable amount of practically pure 9-benzoyl-*cis*-hexahydrocarbazole then separated. After filtration, the alcoholic mother-liquor was added to an excess of aqueous-alcoholic potassium hydroxide, the mixture boiled under reflux for 3 hours, as much alcohol as possible distilled off, and the residual mixture diluted with water. The sticky product was washed by decantation and crystallised from alcohol; almost pure trans-*hexahydrocarbazole* then separated,

On recrystallisation from alcohol, it was obtained in colourless needles (about 12 g.), m. p. 127° (Found: C, 83·2; H, 8·7; N, 8·1. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%). Molecular-weight determinations by Rast's method (*Ber.*, 1922, **55**, 1051) gave for *trans*-hexahydrocarbazole a value of 170 and for the *cis*-form 163, theory requiring 173. *trans*-Hexahydrocarbazole, like the *cis*-modification, is readily soluble in dilute hydrochloric acid and is reprecipitated on addition of ammonia. Both modifications distilled unchanged: *trans*-, b. p. 286°/769 mm.; *cis*-, b. p. 280°/769 mm.

trans-Hexahydrocarbazole (0·5 g.) and picric acid (0·65 g.) were mixed in hot alcohol; the *picrate* separated, on cooling, in yellow needles, m. p. 179° (Found: N, 13·9. $C_{18}H_{18}O_7N_4$ requires N, 13·9%). The *picrate* of the ordinary *cis*-modification, prepared in the same way, was obtained in yellow needles, m. p. 166° (Found: N, 13·7%).

After *trans*-hexahydrocarbazole had been boiled with an excess of acetic anhydride for an hour, the mixture shaken with much water, and the product crystallised from dilute alcohol, 9-*acetyl*-trans-*hexahydrocarbazole* separated in long, colourless needles, m. p. 113° (Found: N, 6·4. $C_{14}H_{17}ON$ requires N, 6·5%). 9-Acetyl-*cis*-hexahydrocarbazole melts at 98° (Graebe and Adlerskron, *Annalen*, 1880, **202**, 25).

When *trans*-hexahydrocarbazole was made into a paste with water, an excess of dilute aqueous sodium hydroxide added, and the mixture shaken with benzoyl chloride, 9-*benzoyl*-trans-*hexahydrocarbazole* separated; it crystallised from alcohol in colourless needles, m. p. 133° (Found: N, 5·2. $C_{19}H_{19}ON$ requires N, 5·1%). The m. p. of 9-benzoyl-*cis*-hexahydrocarbazole is 106° (Gurney and Plant, this vol., p. 1320).

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, October 12th*, 1927.]

CCCLVI.—*The Hydrolysis of Solutions of Sodium Palmitate as measured by Extraction with* p-*Xylene.*

By JAMES WILLIAM MCBAIN and REGINALD BUCKINGHAM.

AFTER long uncertainty and widely conflicting opinions, it is now commonly accepted that the hydrolysis alkalinity of soap solutions is of the order of only $N/1000$ (conductivity: McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179; hydrogen electrode: McBain

and Martin, J., 1914, **105**, 957; catalysis: McBain and Bolam, J., 1918, **113**, 825; Beedle and Bolam, *J. Soc. Chem. Ind.*, 1921, **40**, 27T; ultrafiltration: McBain and Jenkins, J., 1922, **121**, 2325; indicators: McBain and Hay, unpublished). The presence of free fatty acid in all soap solutions is readily demonstrated by shaking them with any suitable solvent such as light petroleum or toluene (Krafft and Stern, *Ber.*, 1894, **27**, 1747, 1755; Krafft and Wiglow, *ibid.*, 1895, **28**, 2566, 2573; Lewkowitsch, *Z. angew. Chem.*, 1907, **20**, 951; Fendler and Kuhn, *ibid.*, 1909, **22**, 107; Holde, *Z. Elektrochem.*, 1910, **16**, 436; S. von Schapringer, Dissert., Karlsruhe, Freiberg, 55—67; Reychler, *Int. Congr. Appl. Chem.*, 1912, **22**, 221), which always extracts fatty acid although the amount is only a small fraction of that which the soap would yield if completely decomposed. As will be seen, such extraction occurs from all soap solutions, whether neutral or containing excess of acid or of alkali. In every case, likewise, the solutions are definitely alkaline even when as much as a complete equivalent of excess of fatty acid has been added to the soap.

Even now, however, the statement is frequently made that soap solutions contain emulsified free fatty acid. This is never true. In spite of the low solubility of the higher fatty acids, there is never enough free fatty acid to saturate the solution, much less to give an excess. If the aqueous layer is saturated with fatty acid, then any non-aqueous layer in equilibrium with it would also be saturated, but in no case has this been observed.

The higher fatty acids must be almost as strong as acetic acid, as is evident from a study of the dissociation constants of the lower acids of the homologous series. The only reason why soap solutions are appreciably hydrolysed is that the free fatty acid formed by hydrolysis is almost wholly removed from solution in the form of acid soap. Such acid soaps form a conspicuous, but often almost unweighable, sediment in dilute soap solutions, and the gross composition of these sediments has often been determined (see McBain and Taylor, *loc. cit.*; Krafft and Stern, *loc. cit.*; McBain, Taylor, and Laing, J., 1922, **121**, 621; McBain and Stewart, this vol., p. 1392), although the elucidation of their exact constitution awaits more rationally planned experiments. There is no similar outlet for the alkali formed by hydrolysis, and it therefore accumulates in the solution. The hydrolysis alkalinity, *i.e.*, the concentration of free hydroxyl ions, is therefore always much greater than the mere trace of free fatty acid present in the solution. Addition of a very small amount of alkali scarcely increases the hydrolysis alkalinity, because it is compensated by removal of acid soap.

It is evident, therefore, that extraction with solvents does not

measure the hydrolysis alkalinity, but that when equilibrium is attained the concentration of the free fatty acid in true solution in the final aqueous layer is indicated. The value of the distribution ratio is such that the concentration of fatty acid in the non-aqueous layer is of the order of 10^6 times greater than that in the aqueous layer. Two kinds of experiments may be carried out, *viz.*, those in which soap solutions are extracted with solvent and therefore changed in composition, and those in which approximately the right amount of fatty acid is previously added to the non-aqueous layer, so that the final equilibrium is determined without appreciable alteration of the aqueous solution. Both methods have here been adopted. When a large excess of fatty acid is added in advance to the non-aqueous layer, it passes into the soap solution, thus again demonstrating the formation of acid soap, since the non-aqueous layer is left unsaturated. It is important that true reversible equilibrium between the two layers was readily obtained in our experiments; the position of equilibrium was obtainable from both sides and did not alter with time at 90°.

Experimental.

All the work was carried out at Bristol University. Mr. H. H. Cole studied toluene, xylene, and deca- and tetra-hydronaphthalene with a view to find a solvent which would fulfil the following conditions: it should be (1) of fairly high boiling point, (2) non-miscible with water, (3) a non-solvent for soap and sodium hydroxide, and (4) only a moderate solvent for fatty acid, which should dissolve as unassociated molecules. He found that the solubility of palmitic acid in twice-distilled *p*-xylene (b. p. 137—138° under 760 mm. pressure) was 33·8 g. in 100 g. of *p*-xylene at 50° and 73·5 g. at 90°, and ebullioscopic measurements showed that the fatty acid was mainly present as simple molecules (Found: *M*, 322, 322, 328, 336. Calc.: 266), but the boiling point constant was found only by calculation. Blank experiments showed that if 9·5 g. of palmitic acid were added to 12 c.c. of xylene, the residue after evaporation showed a loss of only 0·1—0·2 mg. of the acid. Further, xylene was found to dissolve only 0·06% of its weight of sodium palmitate when shaken at 95—97° for 22 hours, thus showing that for the purpose of the present experiments sodium palmitate is insoluble in xylene.

The method here employed is substantially that developed by Miss A. M. King. The greatest practical difficulty is due to the extreme readiness with which these soap solutions become more or less permanently emulsified with the xylene layer, so that separation for analysis becomes impossible. This was finally avoided by carrying out the extraction in horizontal sealed tubes, about

23 cm. long and 1·3 cm. in diameter, tied parallel to the axis of a slowly rotating horizontal stirrer making 20—60 revs. per min. Even under these conditions, if the tubes contained a very large excess of fatty acid or nearly enough salt to salt out the soap, frothing occurred extensively. Between 7000 and 8000 revs. were allowed for attainment of equilibrium, and after 15 minutes' further standing the xylene layer was usually quite clear. Thereupon, the top of the tube was cut off without removal from the thermostat, and as much as possible of the xylene layer was drawn off and weighed; the xylene was then evaporated at 80°, a tube attached to a filter-pump being kept near the surface of the solution in an evaporating dish to renew the air. After 2 hours' drying the residue of fatty acid was weighed.

Two specimens of sodium palmitate, specially made for us by Kahlbaum, were employed. Specimen A contained 4·5% of water and an excess of alkali amounting to 0·0001 equiv. of sodium per equiv. of soap. Specimen B contained 3·47% of water and 0·0008 equiv. excess of sodium. These amounts of alkali and water are allowed for in recording the composition of the solution. All solutions were made with boiled-out conductivity water (1×10^{-6}) in Jena glass flasks. In experiments involving excess of fatty acid or alkali, palmitic acid ("Kahlbaum") or drippings from sodium, free from carbon dioxide, were used, respectively. The salts used were Kahlbaum's "for analysis," dried at 120—130°. Sodium carbonate was heated to bright redness in a platinum crucible for 3 hours. In each case it was found that the salts were insoluble in xylene. All solutions were made up by weight, and concentrations are expressed in weight normality (equivs. per 1000 g. of solvent, water, or xylene). About 7 c.c. of soap solution were used in each experiment. In all cases the temperature was 90° ±0·1°.

Results.

Proof that True Equilibrium is attained.—In order to attach significance to the results, it is necessary to demonstrate that true reversible equilibrium is attained between the two phases. This is conclusively shown by the experiments in Table I, in which identical results were obtained from two series of experiments approaching equilibrium from opposite sides. In the first series, a $0{\cdot}0774N_w$-solution of sodium palmitate was shaken with an approximately equal quantity of pure xylene. In the second series, a $0{\cdot}0774N_w$-solution of sodium hydroxide was shaken with an equivalent quantity of palmitic acid dissolved in xylene. In the first series, after equilibrium had been attained, 17·1% of the total palmitate radical in the system was present in the xylene layer as

palmitic acid. In the second series, 17·3% of the original palmitic acid was finally left in the xylene layer, the remainder having gone into the aqueous layer to react with sodium hydroxide. Thus for the first time it is shown that true equilibrium can be attained in suitably planned experiments on the extraction of soaps.

TABLE I.

Proportion of total palmitate radical extracted when equal weights of 0·0774N_w*-aqueous solution of sodium palmitate and* p*-xylene are brought into equilibrium at* 90°.

Aqueous layer.			Xylene layer.		
N_w-Soap * before.	N_w-NaOH before.	N_w-NaOH † after.	N_w-HP ‡ before.	N_w-HP § after.	% Total HP extracted.
0·0774	0	0·01326	0	0·01262	17·28
0·0774	0	0·01384	0	0·00841	18·01
0·0774	0	0·01257	0	0·01659	16·33
0·0774	0	0·01056	0	0·01397	17·33
0·0774	0	0·01338	0	0·01587	17·43
0·0774	0	0·0100	0	0·01650	16·43
0	0·0774	0·0138	0·0774	0·0138	17·81
0	0·0774	0·0129	0·0774	0·0129	16·69

* Specimen A.

‡ HP = palmitic acid.

† The numbers recorded do not include the hydrolysis alkalinity due to the soap, but only the excess of sodium hydroxide left in the soap solution corresponding with the palmitic acid extracted. The total final alkalinity is not the sum of the original and that shown, because some of the acid extracted comes from acid soap.

§ A saturated solution would be 2·93N_w-palmitic acid.

In order to determine the effects of varying the concentration of soap and the amounts of the aqueous and xylene layers, data are given in Table II for the proportion of the total palmitate radical present in the system which is finally found as palmitic acid in the xylene layer when neutral soap solutions are shaken with xylene.

In all the foregoing experiments the soap solution is robbed of part of its palmitic content by the xylene. Hence the experiments in Table III were carried out by adding excess of palmitic acid to the original xylene, various concentrations being tried until palmitic acid was neither given up to nor extracted from the soap solution. This not only yields the concentration of palmitic acid that is in equilibrium with the unaltered soap solution, but it also affords conclusive proof that true reversible equilibrium was attained in these experiments. The results are plotted in Fig. 1.

Increased experimental difficulties are encountered when the concentration of palmitic acid in xylene exceeds 0·25N_w, *i.e.*, 6%: it was difficult to effect complete evaporation of the xylene if the

TABLE II.

Proportion of total palmitate extracted as palmitic acid when p-*xylene is shaken with aqueous solutions of sodium palmitate at* 90°.

N_w-NaP * before.	Soap soln. (g.).	N_w-NaOH † after.	Xylene (g.).	N_w-HP ‡ in xylene.	% HP extracted.
0·1388	5·2069	0·00684	9·0303	0·01145	4·92
0·1388	6·8610	0·00716	9·0818	0·00915	5·16
0·1388	5·3660	0·00687	7·9261	0·00979	4·94
0·1388	7·4565	0·00793	8·3362	0·00855	5·58
0·1388	6·4728	0·00834	7·7412	0·00857	5·97
0·1118	6·844	0·0109	8·82	0·00821	9·78 §
0·1118	9·396	0·0095	8·82	0·00982	8·50 §
0·1118	7·665	0·0116	8·80	0·00984	10·42 §
0·1096	4·917	0·0144	8·80	0·007877	13·13 §
0·1096	4·501	0·0177	17·60	0·004895	16·15 §
0·1096	4·501	0·0182	17·60	0·004512	16·58 §
0·1096	4·389	0·0177	17·56	0·004295	16·5 §

* Specimen A. † See corresponding footnote in Table I.

‡ A saturated solution would be $2·93N_w$-palmitic acid.

§ Measurements by Miss King, in which the solutions were allowed to stand from 3 to 12 days, thus confirming that time does not appreciably affect the equilibrium at 90°.

TABLE III.

Experiments in which $0·100N_w$-*solutions of sodium palmitate (Specimen B) and water were shaken at* 90° *with xylene to which various amounts of palmitic acid had been added in advance.*

Soap soln. (g.).	Xylene soln. (g.).	HP in xylene. Before, N_w.	HP in xylene. After,* N_w.	Excess in H_2O layer after. NaOH, N_w.	Excess in H_2O layer after. Acid soap, N_w.
5·1691	7·0673	0·1170	0·1217	0·0058	—
4·1934	8·4574	0·1386	0·1385	0·00067	—
6·0092	5·2940	0·1464	0·1452	—	0·0002
4·6990	6·3900	0·1686	0·1655	—	0·0033
6·7521	5·7714	0·1758	0·1704	—	0·0038
5·0572	5·6892	0·1840	0·1790	—	0·0044
5·5903	8·1763	0·1954	0·1909	—	0·0053
5·1498	5·1032	0·2384	0·2310	—	0·0076
4·9988	6·7175	0·9545	0·9371	—	0·0207

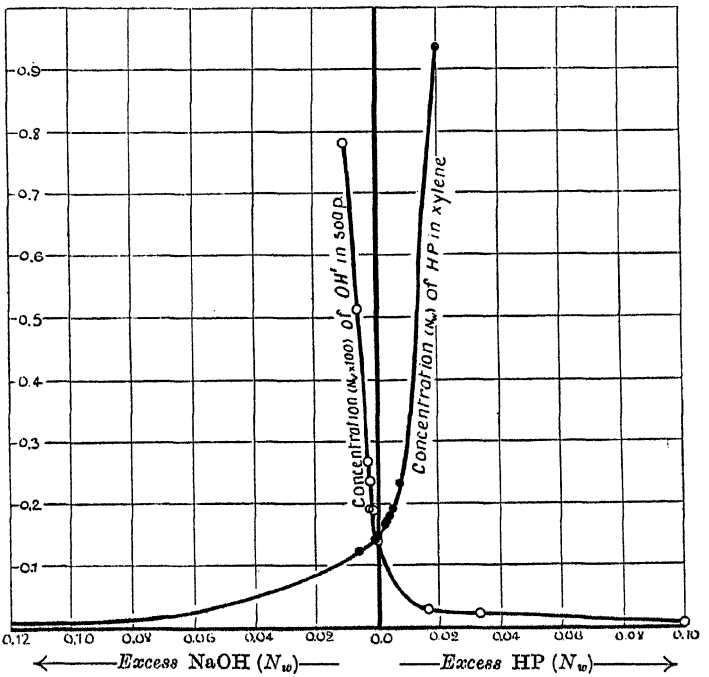
* A saturated solution of palmitic acid would have been $2·93N_w$.

usual amount of solution was used; hence, the solutions were evaporated at 80° under 20 mm. Hg. There is also a strong tendency to emulsification when the xylene contains between 10% and 20% of palmitic acid, but this diminishes again at higher concentrations. The formation of acid soap is indicated by the soap layer becoming absolutely opaque. An experiment with 25% palmitic acid ($0·9545N_w$) is given in Table III and is also included in Fig. 1.

Effect of Electrolytes upon the Extractability.—Table IV and Fig. 2 record experiments in which various pure salts were dissolved in

the $0{\cdot}1N_w$-sodium palmitate solution at 90° before it was shaken with xylene. The salts increased the tendency to frothing, and as the concentration of salt required for salting into two aqueous layers was approached, emulsification became so prominent that the xylene layer finally could not be analysed. The salts made the

FIG. 1.



Hydrolysis equilibria in aqueous sodium palmitate containing excess or deficiency of either sodium hydroxide or palmitic acid. The curve for hydrolysis alkalinity is that obtained by McBain and Martin by the E.M.F. *method. The other curve shows the concentrations of palmitic acid in xylene when the xylene layer is in equilibrium with the soap solution of the final concentration indicated (one experimental point lies off the left of the diagram). Were the palmitate ion constant throughout, the concentrations of hydroxyl ion and of free palmitic acid in the aqueous phase would be inversely proportional to each other.*

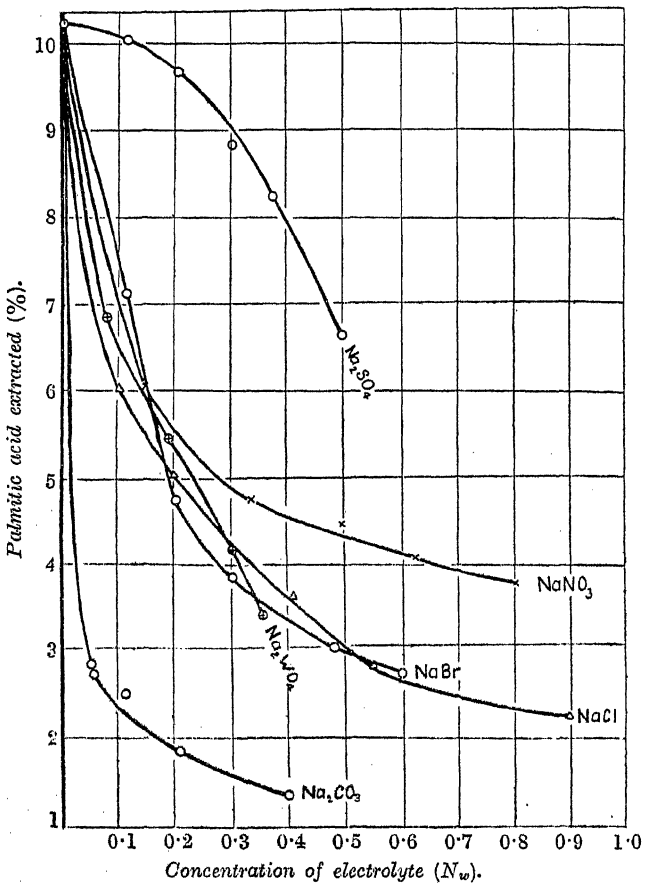
originally clear soap solution cloudy. All the experiments were carried out with Specimen B of sodium palmitate.

Discussion and Interpretation of Results.

The outstanding result of these measurements is that there is scarcely any free fatty acid in a soap solution even when it is appreciably hydrolysed. There is practically quantitative conversion of the fatty acid formed into insoluble acid soap. For

example, a $0{\cdot}1N_w$-solution of exactly neutral sodium palmitate is in equilibrium with the xylene layer containing $0{\cdot}143N_w$-palmitic acid. The saturation concentration or solubility of palmitic acid in xylene is $2{\cdot}93N_w$; hence the xylene layer, and therefore likewise

FIG. 2.



The effect of the addition of salts to aqueous sodium palmitate at 90° upon the amounts of palmitic acid passing into the non-aqueous layer when the soap solution is shaken with an approximately equal volume of p*-xylene.*

the aqueous layer, is not more than 5% saturated with palmitic acid. McBain and Taylor (*loc. cit.*) found the solubility of the undissociated palmitic acid in water at 90° to be $0{\cdot}6 \times 10^{-5}N_w$, and therefore, if the distribution ratio between water and xylene is a constant, the concentration of free palmitic acid in the aqueous layer is only $3 \times 10^{-7}N_w$, whereas the hydroxyl-ion concentration

TABLE IV.

Effect of added salts upon the extractability of $0{\cdot}1N_w$*-sodium palmitate at* 90°.

NaP soln. (g.).	Xylene (g.).	N_w-salt.	N_w-HP in xylene.	% HP extracted.	N_w-NaOH formed.
		Sodium chloride.			
5·3619	5·8108	0	0·00942	10·48	0·0105
5·9920	4·4946	0·1000	0·0112	8·68	0·0086
5·3282	5·0708	0·2000	0·0051	4·96	0·0050
4·7650	6·1778	0·4110	0·0027	3·61	0·0036
4·7140	6·2668	0·5534	0·0020	2·84	0·0028
5·5412	5·1768	0·8970	0·0024	2·30	0·0023
		Sodium bromide.			
5·3619	5·8108	0	0·0094	10·48	0·0105
4·0070	4·8030	0·115	0·0058	7·1	0·0071
6·6604	8·4060	0·204	0·0041	4·4	0·0053
4·5606	6·3834	0·300	0·0034	3·83	0·0048
4·6928	6·1300	0·478	0·0023	3·0	0·0038
4·2768	8·4032	0·600	0·0013	2·67	0·0027
		Sodium sulphate.			
5·3619	5·8108	0·0	0·00942	10·48	0·0105
4·8294	6·3338	0·1145	0·00745	10·05	0·0105
6·3770	5·0828	0·206	0·01204	9·837	0·0098
4·9878	5·4478	0·30	0·00813	8·8	0·00913
5·6500	5·7562	0·376	0·0079	8·34	0·0083
5·7488	6·3568	0·50	0·0058	6·62	0·0066
		Sodium carbonate.			
5·3619	5·8108	0·0	0·00942	10·48	0·0105
6·2130	5·3842	0·100	0·0031	2·8	0·0028
5·8700	6·6298	0·109	0·0023	2·7	0·0027
6·2370	7·4788	0·231	0·0021	2·47	0·00248
5·3062	7·6776	0·417	0·0012	1·80	0·0019
5·4568	7·7641	0·811	0·00086	1·27	0·0012
		Sodium nitrate.			
5·3619	5·8108	0	0·009423	10·48	0·0105
5·5170	5·1642	0·1622	0·0062	5·98	0·0060
5·2456	6·5292	0·337	0·0037	4·70	0·0047
5·5046	6·642	0·475	0·0061	4·4	0·0042
4·606	8·2568	0·634	0·0022	4·0	0·0026
4·8728	6·945	0·809	0·0025	3·72	0·0037
		Sodium tungstate.			
5·3619	5·8108	0	0·00942	10·48	0·0105
5·5227	5·4125	0·1590	0·0067	6·8	0·0068
5·6696	5·2544	0·3828	0·0057	5·4	0·0054
4·2324	5·5602	0·6018	0·0052	4·1	0·0070
5·0958	7·4986	0·7152	0·0022	3·36	0·0034

or hydrolysis alkalinity is $0{\cdot}0013N_w$, as found by several independent methods. Hence, all the palmitic acid representing the difference between these two numbers is removed from solution in the form of acid soap.

It is possible from the data of McBain and Taylor to predict

what concentration of palmitic acid should have been found in $0{\cdot}1N_w$-aqueous sodium palmitate at 90°. Taking the dissociation constant of palmitic acid as 1×10^{-5}, that of water as 33×10^{-14}, the concentration of simple palmitate ion in the solution as $0{\cdot}035N_w$, and the concentration of hydroxyl ion as $0{\cdot}0013N_w$, one can predict the concentration of palmitic acid as $9 \times 10^{-7}N_w$. The $3 \times 10^{-7}N_w$ was estimated above on the assumption that palmitic acid has the same solubility in pure water as it has in $0{\cdot}1N_w$-sodium palmitate saturated with xylene; this is probably not quite correct and may account for the small discrepancy.

The possible influence of salts upon the distribution coefficient, and still more upon the degree of insolubility of acid soap, constitutes the chief uncertainty in interpreting the results in Table IV and Fig. 2. It is clear that the addition of salts to the soap solution diminishes the extractability and probably the hydrolysis, although this should be checked by direct measurement of hydrolysis alkalinity. All these soap solutions were rendered alkaline by the abstraction of palmitic acid, those containing most salt being least affected and yet giving up least palmitic acid. The behaviour of all salts is very similar with the exception of sodium carbonate and sodium sulphate; the difference in the case of the former is clearly due to its alkalinity, but no explanation is forthcoming as to the peculiar shape of the curve for sodium sulphate unless the salt was slightly acid, which was not tested at the time. The effect of the various salts bears no relation to their effect upon salting out of soaps, to the Donnan equilibrium, or to the Hofmeister series, and shows no influence of valency, because all the salts replace each other mol. for mol. with the exception of the carbonate and sulphate. The effect is undoubtedly due to diminution in the concentration of simple palmitate ion (the substance that hydrolyses) and its replacement by colloid. The same explanation would account for the rapid fall in the % hydrolysis with increasing concentration of soap as is illustrated in Table II; 17% of the total palmitate in $0{\cdot}0774N_w$-solution was extracted by an equal amount of xylene, whereas from a solution of twice the concentration only 5% was extracted.

In conclusion, attention may be directed to the series of buffer reactions which occur within a soap solution and render its hydrolysis alkalinity less dependent upon extraneous additions than is usually the case with standard buffers. For example, large change of concentration of the soap, addition of acid or even of a small amount of alkali, and variation of the amount of any non-aqueous solvent with which the solution is shaken all effect only a small change in the concentration of hydroxyl ion. The hydrolysis is chiefly regulated by the insolubility of the acid soap, which is

greatest for the highest fatty acids and distinctly less for unsaturated fatty acids. Further experimental work is now in progress at Stanford University.

Summary.

1. Contrary to the opinions hitherto expressed by most writers, no soap solution contains more than the merest trace of uncombined fatty acid, and even that is completely dissolved, none being in the emulsified or free condition. Thus, in spite of the sparing solubility of the higher fatty acids, soap solutions are unsaturated with respect to them. This is conclusively proved by the fact that any non-aqueous solution brought into equilibrium with an aqueous soap solution is very far from being saturated with fatty acid, even when a large excess of the acid has originally been added to the system.

2. Practically all of the fatty acid corresponding to the hydrolysis alkalinity is locked up in combination as (insoluble) acid soap. Soap solutions are excellent buffers.

3. Electrolytes, even up to high concentrations, diminish the extractability, and probably the hydrolysis, of dissolved soap.

STANFORD UNIVERSITY, CALIFORNIA. [*Received, August 18th*, 1927.]

CCCLVII.—*The Effect of Electrolytes upon the Viscosity of Solutions of Sodium Palmitate.*

By JAMES WILLIAM MCBAIN, HERBERT JAMES WILLAVOYS, and HAROLD HEIGHINGTON.

MANY investigators have studied the viscosity of soap solutions and the effect of electrolytes thereon (Mayer, Schaeffer, and Terroine, *Compt. rend.*, 1908, **146**, 484; Bottazzi and Victoroff, *Atti R. Accad. Lincei*, 1910, (v), **19**, i, 659; Farrow, J., 1912, **101**, 354; Goldschmidt and Weissmann, *Z. Elektrochem.*, 1912, **18**, 380; *Koll. Z.*, 1913, **12**, 18; *Seifensieder Ztg.*, 1913, **40**, 263; Hatschek, *Koll. Z.*, 1913, **12**, 238; *Trans. Faraday Soc.*, 1913, **9**, 80; Kurzmann, *Koll.-Chem. Beih.*, 1914, **5**, 427; Arndt and Schiff, *ibid.*, 1914, **6**, 201; Goldschmidt, *Seifensieder Ztg.*, 1914, **41**, 337; Fischer and Hooker, *Chem. Eng.*, 1919, **27**, 223; Clarke, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **6**, No. 1, 1; King, *J. Soc. Chem. Ind.*, 1922, **41**, 147T; Bircumshaw, J., 1923, **123**, 91; Prasad, *J. Physical Chem.*, 1924, **28**, 636; Freundlich and Schalek, *Z. physikal. Chem.*, 1924, **108**, 153; Freundlich and Kores, *Koll. Z.*, 1925, **36**, 241; Jajnik and Malik, *ibid.*, p. 322; Hahne, *Z. deut. Oel-Fett Ind.*, 1925, **45**,

245, 263, 274, 289, 308), but their work has always been broken off in the region where the viscosity was rising rapidly with increasing concentration of added salt. It remained for Miss A. M. King, in a communication from Bristol University (*J. Soc. Chem. Ind.*, 1922, **41**, 147T), to discover the remarkable fact that further addition of salt produces a sharp maximum of viscosity, which thereafter falls rapidly with still further addition. The last effect continues right up to the limit of possible existence of the soap solution as a single homogeneous phase. The present paper gives further information with regard to this effect (see, *e.g.*, Fig. 1).

Solutions of sodium palmitate at 80° and 90° were chosen for study because of the large amount of other information already available, and also because their properties are independent of time at these high temperatures.

Once again it is shown that, if sufficient care is taken to control the factors involved, even such a property as the viscosity of soap solution is definite and reproducible. For example, we have taken the viscosity of a solution $0{\cdot}5N_w$ with respect to both sodium chloride and sodium palmitate at 81·0° as a point of reference. Miss King published the values for its absolute viscosity in c.g.s. units, $\eta = 10{\cdot}63$ and 10·54; one of us (H. J. W.) obtained 10·07, another (H. H.) 10·06, and Mr. H. Horwood 10·39, all with different specimens of pure sodium palmitate. In other series of experiments, the viscosity of the original soap solution was first taken, then successive amounts of pure electrolyte were added, thus giving a range of viscosity readings up to the limit of existence of isotropic soap solutions. Thereupon, the final solution was diluted with successive portions of the original soap solution, retracing the curve, and yielding confirmatory values.

For details of the experimental method reference may be made to the communication cited. A Wenner stop-watch reading to 0·01 sec. was employed. Temperatures were read on standardised thermometers. The steel balls required were heated before being dropped through the tube in order to avoid solidification of the soap solution on them. All concentrations are expressed in weight normalities (N_w), *i.e.*, g.-mols. per 1000 g. of water.

The results were calculated according to the formula $\eta = K(s - D)T$, where K is the tube constant $\eta_1/(s - \sigma)T_1$, η is the viscosity of the soap solution in c.g.s. units, D its density, s the density of the steel ball, T and T_1 are the times of fall in soap solution and castor oil respectively, η_1 is the viscosity of castor oil = 16·46 c.g.s. units at 14·1°, and σ the density of castor oil = 0·963. The value of K depends upon the dimensions of the tubes and balls, and the values used are given in Table I.

TABLE I.

Calibration of the falling balls and tubes with castor oil (Kahlbaum).

Observer.	Temp.	Diam. of steel balls.	Density of balls.	T_1 (secs.).	Tube constant, K.
Horwood	14·1°	0·316 cm.	7·595	6·0	0·4136
„	14·1	1/8 in.	7·720	6·2	0·3928
Heighington	14·1	1/8 in.	7·697	6·2	0·3943
Willavoys	15·7	0·163 cm.	7·554	29·32	0·0731

The results for 0·75, 1·0, and $1{\cdot}5N_w$-solutions of sodium palmitate with added sodium chloride are in Table II. The $1{\cdot}5N_w$-solutions are so viscous that for determining the density a specially wide pipette was employed, closed at the bottom with a flattened glass rod held in place by rubber tubing, and continued at the top with a small tube also held in place by rubber tubing so that when temperature equilibrium was attained this could be slipped off, leaving the pyknometer exactly filled with soap solution. Thereupon the tube was cooled and the contents were solidified for weighing.

Results for approximately $1{\cdot}5N_w$-sodium palmitate with added sodium carbonate or acetate at 81° are given in Table III.

Discussion.

The experimental results for added sodium chloride at 81° are shown in Fig. 1 and those for the acetate and carbonate in Fig. 2. The outstanding effect is that the addition of medium concentration of electrolyte enormously increases the viscosity of soap solution. Without salt, the viscosity is only a few centipoises, and it is increased 600—700-fold at the maxima by the addition of the salt. It may be recalled that with many soaps at lower temperatures the soap solutions in these intermediate concentrations of salt actually set to a jelly, but the effect there also passes through a maximum, and further addition of salt reliquefies the jelly.

The most striking feature of the curves is the existence of these sharp maxima at which the effect of salts is reversed, the viscosity with further increase of salt falling off as rapidly as it had risen. For example, in the curve for carbonate (Fig. 2) the highest viscosity measured was 102 poises, which fell on further addition of carbonate to 6 poises. With the most concentrated soap and sodium chloride, the fall is from 55 to 3 poises. The limited extent of the fall is, however, shown by the fact that when the soap solution contains all the salt that can be added without the formation of several layers, the viscosity is still 20—50 times higher than that of the original soap without salt.

TABLE II.

Viscosity and density of solutions of sodium palmitate containing various weight normalities of added sodium chloride at about 81·0°.

Observer.	Temp.	NaCl (N_w).	T (secs.).	Density (g./c.c.).	η.
		0·75N_w-Sodium palmitate.			
Horwood	81°	0·729	2·5	0·992	6·82
,, ...	,,	0·600	5·3	0·991	14·48
,, ...	,,	0·748	2·4	0·991	6·34
H. H.	,,	0·201	0·9	0·977	2·38
,, ...	,,	0·400	7·6	0·9850	20·11
,, ...	,,	0·500	6·99	0·9877	18·49
,, ...	,,	0·300	3·39	0·9823	8·96
,, ...	,,	0·600	5·2	0·9900	13·75
,, ...	,,	0·450	8·718	0·9864	23·07
H. J. W.	,,	0·440	57·74	0·981	27·74 *
,, ...	90	0·880	1·79	0·9872	0·73 †
		1·0N_w-Sodium palmitate.			
H. H.	81·00	0·880	0·98	1·00000	2·59
,, ...	81·26	0·6797	3·06	0·99805	8·08
,, ...	81·7	0·5771	5·42	0·99570	14·4
,, ...	81·63	0·46945	7·3	0·98805	19·3
,, ...	81·64	0·50000	7·24	0·98980	19·1
,, ...	81·65	0·37220	9·95	0·98645	26·3
,, ...	81·68	0·26205	11·23	0·98310	29·7
,, ...	81·76	0·14445	4·17	0·97910	11·0
,, ...	81·7	0·29000	10·47	0·98310	27·7
,, ...	81·7	0·25000	7·7	0·97530	20·4
,, ...	81·7	0·32000	11·1	0·98470	29·4
H. J. W.	80·96	0·3000	68·76	0·9826	33·0
,, ...	90·05	0·3000			10·2
H. H.	81·92	0·1445	4·76	0·9791	12·3
		1·50N_w-Sodium palmitate.‡			
H. J. W.	80·97	0·100	88·21	0·9740	39·54
,, ...	80·95	0·7500	11·60	1·005	5·55
,, ...	80·99	0·8700	6·45	1·016	3·08
,, ...	81·01	0·7120	12·45	1·001	5·96
,, ...	81·00	0·5658	26·06	0·9965	12·48
,, ...	90·06	0·4395	17·16	(0·9851)	8·24
,, ...	81·01	0·4395	41·53	0·9851	19·94
,, ...	81·03	0·3015	71·03	0·9614	34·23
,, ...	90·05	0·2660	29·75	0·9614	14·33
,, ...	81·00	0·2660	75·78	0·9458	36·59
,, ...	81·00	0·2431	85·38	0·9806	41·02
,, ...	80·99	0·2032	102·77	0·9651	49·49 §
,, ...	81·01	0·1845	105·27	0·9642	50·71 §
,, ...	81·00	0·1459	109·43	0·9692	52·65 §
,, ...	80·98	0·1049	83·48	0·9800	40·12
,, ...	80·94	0·08076	67·77	0·9740	32·59
,, ...	80·98	0·06503	83·32	0·9700	40·09
,, ...	81·02	0·04287	83·58	0·9600	40·28

* High value owing to slight fall in temperature.

† At 90°, hence about 2·2 at 81°.

‡ 1·5N_w-Sodium palmitate does not exist as a single homogeneous solution at 81°, but falls in the heterogeneous region—middle soap + isotropic solution (see McBain and Langdon, J., 1925, **127**, 863).

§ Small crystals developed (acid sodium palmitate).

TABLE III.

Viscosity and density of solutions of sodium palmitate containing various weight normalities of added salts at about 81°.*

Temp.	Added salt (N_w).	T (secs.).	Density (g./c.c.).	η.
	1·491N_w-Sodium palmitate with addition of sodium carbonate.			
81·05°	0·1876	213·3	(1·000)	102·2
81·09	0·4764	108·0	1·016	51·50
80·99	1·2736	26·8	(1·000)	12·84
80·99	1·6228	12·54	(1·000)	6·01
	0·1000	Heterogeneous—two layers.		
	1·47N_w-Sodium palmitate with addition of sodium acetate.			
81·01	0·09786	90·82	0·9712	43·69
81·02	0·1490	118·85	0·9815	57·12
81·02	0·2081	128·97	0·9825	61·95
81·01	0·2759	67·23	0·9842	32·28
81·00	0·3958	27·50	0·9851	13·20
	0·5837	Heterogeneous system—nigre and lye.		

* Experiments by H. J. W.

The higher the concentration of soap, the less salt is required to produce the maximum viscosity, as the following tabulation shows :

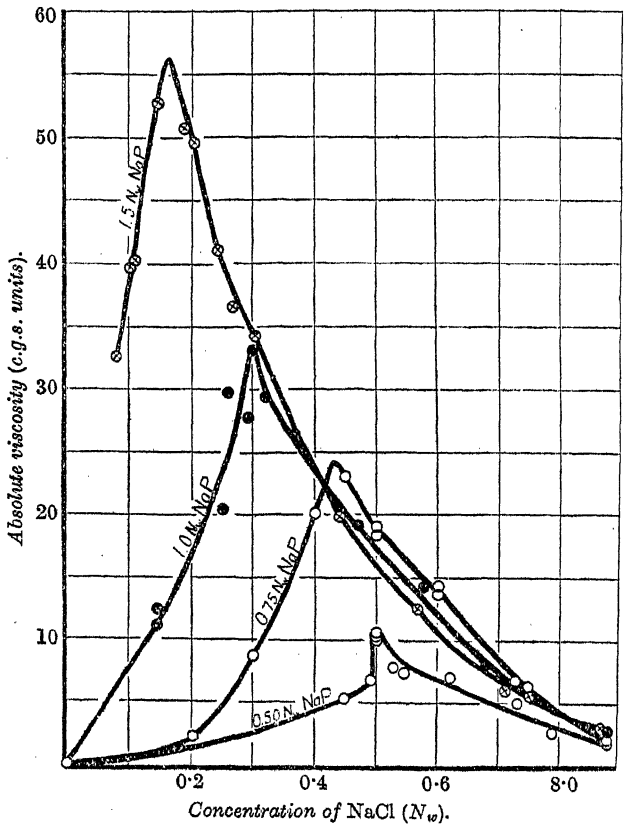
Conc. of soap (N_w)	0·5	0·75	1·0	1·5
Max. viscosity (poises)	10	24	33	56
Conc. (N_w) of salt at max. viscosity	0·50	0·43	0·30	0·16

The enormous increase in viscosity of a soap solution when moderate quantities of salt are added to it again shows the inadequacy of the emulsoid theory of colloids. In these strong soap solutions the soap is all in colloidal form already, before any salt is added. According to the emulsoid theory, addition of salt should shrink the globules of soap, and the viscosity should be diminished instead of being increased many hundred-fold. That the salt is less soluble in a soap-rich phase has been definitely proved by the numerous studies of phase-rule equilibria now available, and, indeed, by the experience of any soap boiler. This affords, therefore, yet another reason for replacing the emulsoid hypothesis by the view that the colloidal soap in solution is present in the form of solid particles or micelles.

Superficially, the curves look like any of Loeb's for the Donnan equilibrium. However, they differ in two respects. In the first place, Loeb's experiments never involved more than a five-fold increase in viscosity, whereas these involve increases of a higher order of magnitude. In the second place, Loeb's maxima arose from the fact that he was adding an acid or an alkali to an amphoteric colloid and producing colloidal electrolyte with high conductivity, osmotic activity, etc., whereas here, salts are being added and should have a uniformly depressing action on the viscosity, as was indeed observed by Loeb for salts when added to the systems he studied.

The problem then is to explain why fully formed colloid may have its viscosity increased many hundred-fold through the addition of salt. The only possible explanation seems to be the general hypothesis advanced by one of us (McBain, *J. Physical Chem.*, 1926, **30**, 239), that the viscosity of a reversible colloid, such as nitro-

FIG. 1.



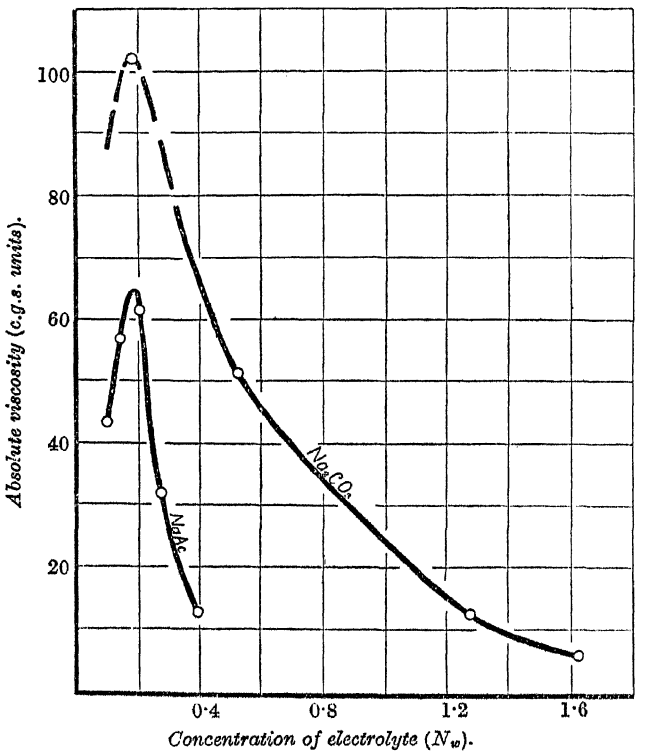
The viscosity of solutions of sodium palmitate at 81° *as affected by addition of sodium chloride up to the maximum amount which can be added without salting out the solution into two layers.*

cotton, soap, rubber, or protein, is not to be accounted for by the individual particles (micelles) either through their number or individual bulk, but that it is due to their loose aggregation into structures which effectively enmesh large tracts of the solvent or solution.

Hatschek (*J. Physical Chem.*, 1927, **31**, 353) has recently published a communication which is ostensibly an attack upon McBain's

general hypothesis of aggregation, but which is really an adoption and endorsement of one particular form of the general hypothesis, being a modification of that of Loeb. In general, there is a great variety of possible forms of aggregation. For example, if all the particles were to be joined end to end to form innumerable filaments, the medium in which they lay could be so effectively enmeshed as to

FIG. 2.



The viscosity of solutions of $1{\cdot}5N_w$*-sodium palmitate at* 81° *over the whole range of existence of isotropic solution in the presence of sodium acetate and sodium carbonate, respectively.*

have the properties of a jelly. Another form of loose ramifying aggregation is that of a pile of brushwood, or again seaweed in a rock pool. Hatschek would prefer to specify only one kind of ramifying aggregate like a lot of separate bushes not entangled but separate from each other, so that each aggregate could be treated approximately as a polyhedron, or even as a sphere. To call this loose ramifying aggregate the micelle is to introduce fresh confusion into the subject. We should prefer to retain the general hypothesis,

which includes Hatschek's as one possibility. We use the term micelle to indicate each of the single ultimate particles of colloid.

Attention may be directed to another influence which greatly enhances the effect of the presence of either particles or ramifying aggregates in their influence upon the apparent viscosity of the system. Hatschek has demonstrated that even in a suspension in which aggregation does not occur and in which hydration in the chemical sense is absent, the system does not show a true viscosity coefficient like a pure liquid, but the viscosity coefficient obtained is a function of the rate of shear. He has been at a loss to account for this effect, and similarly Porter and Rao (*Trans. Faraday Soc.*, 1927, **23**, 311) were unable to offer an explanation, but made a purely empirical attempt to obtain an equation to fit the results. As part of a general theorem relating to the structure of surfaces, one of us (J. W. McB.) and G. P. Davies (Address to the Mid-West Regional Meeting of the American Chemical Society, Madison, June, 1926; *J. Amer. Chem. Soc.*, 1927, **49**, 2230) have shown that this effect is a necessary result. On the basis of accurate absolute measurements on the amount of adsorption, now available for the first time, and of a survey of the results obtained in such fields as that of adhesives, etc., the authors concluded that any surface possesses considerable depth due to chains of oriented molecules extending inwards from points on the outer unimolecular layer. The effective length of these chains is conditioned by thermo-vibration and, of course, by rate of shear, the latter accounting for the results obtained by Hatschek and Porter. Hence a liquid in the neighbourhood of surfaces such as those of particles, filaments, or ramifying aggregates is semi-rigid, enhancing greatly the effectiveness of the aggregates in immobilising liquids, and producing a high apparent viscosity.

According to previous studies of soap, it is the neutral micelle, and not the ionic micelle, that has the power of forming ramifying aggregates. Salt does promote the formation of neutral micelles at the expense of ionic micelles, but this effect is too unimportant for our present purpose. We should ascribe the aggregation of the neutral micelles to partial dehydration on the addition of salt owing to the lowering of the vapour pressure of the solution. This is the first main factor involved in the action of salts upon soap solutions.

The maximum and the subsequent lowering of viscosity have still to be explained, and any explanation has to be sufficiently general to account for the salting out and phase-rule equilibria of soap, together with the formation of liquid crystals. We would seek this in a combination of the principles of dehydration through lowering

of vapour pressure (as above), of orientation of like molecules when held sufficiently close together, and of the principle underlying the Donnan equilibrium. The dehydration facilitates aggregation by exposing unsaturated valence bonds (compare McBain, *J. Physical Chem.*, *loc. cit.*), thus tending to make the aggregates denser and less voluminous. The principle of constancy of ionic product, as exemplified by solubility of precipitates, utilised by Donnan and generalised by Wilson, must now be made use of to explain further the effect of salts upon the charges and the volumes within the colloidal aggregates.

Almost all surfaces, even those of the neutral micelles, show slight electrical charges (see Laing, *J. Physical Chem.*, 1924, **28**, 673). Particles of like charge tend to repel each other, probably not merely through direct electrostatic repulsion (the usual belief), but also through the excess osmotic pressure set up in the neighbourhood of all charges through the Donnan equilibrium. The effect of large excess of salt is two-fold: first, to reduce these charges, and, secondly, to minimise their effect upon the Donnan osmotic pressure in their neighbourhood. These two influences contribute to the collapse, or rather the closer packing, of the structures built up from the micelles, thus reinforcing the effect of increased intensity of aggregation. This releases a part of the liquid, or better, less of it is immobilised, and hence the apparent viscosity falls. This would appear to explain the decline in viscosity that occurs in more concentrated solutions of salts, whilst still leaving the viscosity higher than that of the original soap solution. This explanation embraces that given by Laing and McBain (J., 1920, **117**, 1507) for the formation of true soap jellies which occur in the middle of the isotropic region and are liquefied by excess of added salt. It should be noted that the curves in Fig. 1 cover practically the whole field of the possible existence of isotropic solutions of sodium palmitate (compare McBain and Langdon, *loc. cit.*). Throughout, the chief factor involved in apparent viscosity of colloids is the extent to which the solution or solvent is immobilised through entanglement in colloidal structures.

When aggregation, brought about through dehydration and segregation as detailed above, becomes extreme, and the micelles are therefore more tightly packed in clumps, the tendency towards orientation must strongly assert itself (orientation of molecules accounts for the existence of micelles in the first place). Excess of salt always produces neat soap and lye, the latter being an ordinary salt solution containing most of the salt and scarcely any soap; the neat soap is liquid crystal. The common feature of all present hypotheses regarding the structure of liquid crystals is that they are

full of tracts in which molecules or micelles are in an approximately parallel arrangement.

Whilst the above description appears to afford a reasonable explanation of the phenomena here discussed, searching tests are required to afford independent proof of the truth of each of the mechanisms involved. Again, far too little is known with regard to the structure of liquid crystals. Indeed, soap solutions afford the only examples of liquid crystals readily accessible for experimental study. The position of middle soap has still to receive adequate explanation. If a soap solution containing no added salt is sufficiently concentrated, middle soap separates as a new phase, and, within a certain range of concentration, soap solutions consist only of this form. Middle soap is a colloidal electrolyte, just like the isotropic solutions it has replaced. A small amount of salt may be added to middle soap, but it is destroyed by further salt, being replaced by isotropic soap solution. This is the significance of the curves for $1{\cdot}5N_w$-sodium palmitate in Figs. 1 and 2, which necessarily have their beginning as shown in the diagrams in the presence of the necessary minimum of salt. The pure $1{\cdot}5N_w$-sodium palmitate is middle soap; it turns into isotropic soap solution upon the addition of the requisite amount of salt, and the viscosity shortly thereafter passes through a maximum as shown in the diagrams. It throws a severe strain upon our explanation (detailed above) to account for these phenomena, because they ended in the production of liquid crystal through excess of salt, with the elimination as a separate phase of most of the water and salt, whereas here the $1{\cdot}5N_w$-sodium palmitate begins as liquid crystal, although retaining all the water with it in one homogeneous phase.

The existence of middle soap as liquid crystal is quite evidently due to mere contiguity of the particles on account of the very high concentration of soap. We have to suppose that this orientation is almost tantamount to coalescence, because no negative ions, other than a trace of hydroxyl ion (and of course the ionic micelles), are present to keep the particles apart. Addition of a small amount of salt supplies this defect, and the tracts of parallel orientation are disbanded with the formation of isotropic solution, although the apparent viscosity is already extremely high and aggregation or linkage is already at an advanced stage. Thereafter, but little salt is required to produce the maximum and the other specified effects.

Comparison of the effects due to the three salts is interesting, but in view of the explanations above it cannot be expected to be of direct significance. The two univalent salts, chloride and acetate, are fairly similar in the position and value of the maximum viscosity,

that for sodium acetate being slightly higher and requiring rather more acetate, sodium acetate being a weaker electrolyte than sodium chloride. The bivalent sodium carbonate gives twice as high a maximum viscosity as the chloride and twice as much of it is required for salting out the palmitate into two layers. However, the acetate is exceptionally effective in salting out, $0{\cdot}57N_w$ being sufficient as compared with $0{\cdot}88N_w$ for the chloride and $1{\cdot}7N_w$ for the carbonate. McBain and Pitter (J., 1926, 893), in comparing a large number of salts, pointed out that apparently the single factor most effective in salting out is the concentration of the sodium ion. We suspect that the high viscosity in the presence of the carbonate may be due to its alkalinity, because we have found with various other samples of sodium palmitate that a slight excess of alkalinity very greatly increases the viscosity. Thus, if the sodium palmitate contains about one equiv. per cent. excess of sodium hydroxide, all the maxima of viscosity are roughly 1·7 times greater.

The futility of attempting to apply any of the usual empirical formulæ to our results is evident from the shape of the curves and also from the fact that the right-hand descending portions of the viscosity curves approximately coincide, *i.e.*, the viscosities are there nearly independent of the amount of soap present.

All the work here described was carried out at the University of Bristol.

Summary.

1. The viscosity of solutions of sodium palmitate has been studied over most of the range of existence of isotropic soap solutions in the presence of sodium chloride, acetate, and carbonate.

2. Addition of electrolytes increases the viscosity to a maximum value many hundred times greater than that of the original soap solution. Further salt decreases the viscosity almost equally rapidly until the salting out concentration is reached.

3. The results are discussed on the basis of the general explanation put forward by McBain for the high apparent viscosity of reversible sols and jellies. The rise in viscosity is in the opposite direction to that predicted by the Donnan equilibrium, and exceeds by a hundredfold the viscosity effects observed by Loeb, although the Donnan equilibrium may well be one of the factors involved.

STANFORD UNIVERSITY, CALIFORNIA. [*Received, August 18th*, 1927.]

CCCLVIII.—*The Composition of Bleaching Powder. Part I.*

By EDMUND ARTHUR O'CONNOR.

THE exact composition of the substances contained in bleaching powder has long been a subject for discussion (see Lunge, "Sulphuric Acid and Alkali," 3rd edn., III, pp. 577—587; Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," II, pp. 262—265), which has centred chiefly around the question of the existence of a definite compound of calcium hypochlorite and calcium chloride in equimolecular proportion, to which was usually assigned the constitution CaCl·OCl. Basic compounds containing hypochlorite and chloride have also been postulated by several authors. Lunge (*op. cit.*, p. 585) expressed the following opinion: "It is certain that no calcium chloride is present as such in ordinary bleaching powder." Similar views were held by O'Shea (J., 1883, **43**, 410) and by Orton and Jones (J., 1909, **95**, 751).

A study of the literature led to the conclusion that there is no positive evidence for the existence of a compound of calcium hypochlorite and chloride. Such a compound has never been isolated, and the evaporation at low temperature of solutions obtained by extraction of bleaching powder with water led to a separation of crystals of hydrated calcium hypochlorite, reported as $Ca(ClO)_2,4H_2O$ (Kingzett, J., 1875, **28**, 404; Orton and Jones, *loc. cit.*). At the same time, Orton and Jones obtained three crystalline preparations, containing calcium hypochlorite and chloride together with calcium oxide and water, which on analysis yielded a molecular ratio of hypochlorite to chloride of 1 : 1. These substances, which could not be recrystallised from water, were only approximately analysed, owing to the small quantities available and to the difficulty of complete separation from mother-liquor. There is, therefore, no certainty that any of them was a single definite compound, although it appears likely that one or more basic double salts may exist.

The preparation of calcium hypochlorite comparatively free from calcium chloride, and in some cases free from calcium oxide, has been exploited in recent years by the Chemische Fabrik Griesheim-Elektron (B.PP. 17859, 182927, 188662; D.R.-PP. 188524, 195896, 282746). Calcium hypochlorite, prepared by chlorinating a paste of calcium hydroxide and water and removing as much as possible of the mother-liquor, is stated to be a very stable compound when thoroughly dry, and superior in this respect, as well as in available chlorine, to the best ordinary bleaching powder. Basic compounds

containing 1—4 mols. of calcium hydroxide to one of hypochlorite, prepared by a similar process, are claimed to have the same advantages. Two of these compounds, $Ca(ClO)_2,2CaO,2H_2O$ and $Ca(ClO)_2,4CaO,4H_2O$, were isolated, but not in crystalline condition.

The problem of the exact nature and proportions of the substances composing any particular sample of bleaching powder cannot be expected to be capable of solution, for there is no certainty that equilibrium has been established. The equilibrium composition of a bleaching powder giving any particular ultimate analysis (neglecting formation of chlorate) could be determined if data for equilibria in the quaternary system $Ca(ClO)_2$–$CaCl_2$–CaO–H_2O at the same temperature were available. Consequently, it was decided to attempt at a suitable temperature a preliminary investigation of the three ternary systems in which water is a component.

Solutions of hypochlorites decompose rapidly at the ordinary temperature only in the presence of hypochlorous acid, and if this be removed by addition of a slight excess of alkali, the solutions are comparatively stable, forming chloride and chlorate and evolving oxygen very slowly (Foerster and Jorre, *J. pr. Chem.*, 1899, **59**, 53; Foerster, *ibid.*, 1901, **63**, 141). Solutions of calcium hypochlorite which can contain only small concentrations of free hydroxide rapidly increase in stability as the temperature falls, partly because of the usual diminution of reaction rate and partly because less hypochlorous acid is formed by hydrolysis. The whole of the experimental work was therefore carried out at 0°, and in the system $Ca(ClO)_2$–$CaCl_2$–H_2O a minute amount of calcium hydroxide was allowed to be present in the solutions.

Experimental.

A. *Analytical Methods.*—Hypochlorite was estimated by the usual iodometric method, and chloride by the Volhard process if hypochlorite was absent. In the presence of hypochlorite, chloride was estimated by first determining the former, and then finding the total chloride present after the hypochlorite had been reduced by neutral hydrogen peroxide. The same method of reduction was employed when it was necessary to estimate hydroxide in the presence of hypochlorite. The accuracy of these methods was checked by a determination of total calcium by the oxalate–permanganate process in a few control experiments.

B. *The Preparation and Properties of Calcium Hypochlorite.*—The following procedure, based upon the process of the Chemische Fabrik Griesheim-Elektron (*loc. cit.*), was adopted. About 224 g. (4 g.-mols.) of calcium oxide, prepared by ignition of the pure

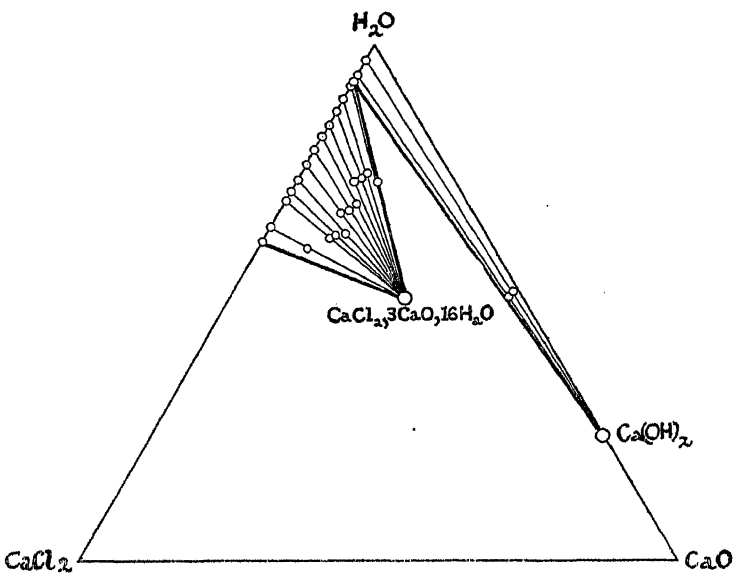
precipitated carbonate, were treated with 650 c.c. of water, whereby a thin paste resulted, quite free from lumps. The cooled paste was introduced into a cylindrical gas-jar provided with a rubber stopper with holes for an inlet tube and a stirrer. The inlet tube reached well down into the jar, and the stirrer, which was of anchor-shape, was made long and wide enough to agitate the whole contents of the cylinder when rotated rapidly by a motor. Chlorine, washed with water, was supplied from a small battery of diaphragm cells, with hydrochloric acid as electrolyte, at an initial rate of about 105 g. per hour. The temperature was allowed to rise to about 40°, external cooling being used when necessary. Under these conditions, there was no visible indication of basic salts, the calcium hydroxide progressively disappearing. After about 70% of the theoretical quantity of chlorine had been admitted, a sudden separation of calcium hypochlorite occurred, and the contents of the flask became pasty once more. The temperature was then reduced to about 25°, and more chlorine was passed in at one-third of the above rate, until from 90% to 95% of the theoretical quantity had been supplied. (After the separation of calcium hypochlorite, chlorine is not absorbed so readily, and a more rapid stream of the gas is partly wasted.) It was not found practicable to chlorinate beyond the limit given, as any further quantity of chlorine caused the complete loss of the preparation by production of free hypochlorous acid.

The paste containing calcium hypochlorite was collected in a Buchner funnel on asbestos-paper, since ordinary filter-paper was rapidly destroyed. The filtration was somewhat slow, but when the characteristically soft mass was covered with asbestos-paper and well pressed, a fair separation from mother-liquor was effected. Comparatively little hypochlorite remained in solution. Further separation of mother-liquor was brought about by pressing the cake of hypochlorite between very thick plates of porous earthenware, specially made for the purpose. After a few hours, the apparently dry substance was desiccated in a vacuum over caustic soda. It formed pale greenish-yellow, almost odourless, apparently non-crystalline lumps, which developed a strong smell of hypochlorous acid on exposure to air.

Pure calcium hypochlorite was prepared by making a saturated solution of the crude product in water and filtering off the insoluble residue of calcium hydroxide or basic salt. The solution was evaporated under the diminished pressure afforded by a water-pump. Concentration progressed until the liquid was considerably supersaturated, and short, needle-shaped crystals finally appeared, at first slowly, then more rapidly. At this stage it was found best

to stop the evaporation, and allow the crystals to be produced without agitation. A more granular product, easily filtered and dried as described above, then resulted. A repetition of the process yielded calcium hypochlorite free from chloride, and therefore free from chlorate. About ½% of calcium hydroxide (or an equivalent quantity of basic salt) was present, rendering unfiltered solutions slightly turbid. Analysis of the final product gave results for hypochlorite and total chlorine which agreed with one another within the limits of experimental error. When thoroughly desiccated, calcium hypochlorite shows no appreciable decomposition

FIG. 1.



after several days, if kept out of contact with air. Concentrated aqueous solutions are greenish-yellow, and decompose at 25—35° at the rate of about 1% per day, evolving a very slow stream of oxygen in minute bubbles. At 0°, there is no decomposition or evolution of oxygen during the period of the experiments.

C. *The System* $CaCl_2$–CaO–H_2O.—This system has already been examined at 10°, 25°, 40°, 48°, and 50° (Milikan, *Z. physikal. Chem.*, 1917, 92, 59), basic compounds $CaCl_2,3CaO,16H_2O$; $CaCl_2,CaO,2H_2O$; and $CaCl_2,CaO.5(?4)H_2O$ being reported. The third was obtained only at 48° and 50°, whilst the range of existence of the first increases and that of the second diminishes as the temperature falls. The results (Table I and Fig. 1) obtained at 0° show that $CaCl_2,3CaO,16H_2O$

is the only basic salt obtainable at that temperature It forms well-defined, transparent, needle-shaped crystals, which may attain a length of several mm. if the mother-liquor does not contain too much calcium chloride.

Suitable complexes were rotated in a thermostat for about 24 hours, which was found to be a sufficient time for establishment of equilibrium, and the composition of the solid phases was deduced by the residue method. The separation of residues from solutions was achieved in the following manner. The disc of a Gooch crucible was placed in the bottom of a small cylindrical funnel and covered with a pad of asbestos well pressed down, which was then thoroughly dried. The funnel was stoppered loosely, fitted to the neck of a filter-flask connected to the water pump, and immersed in the ice and water of the thermostat, only the top projecting. The filtration could then be carried out at 0°, no matter how slowly the solution drained through the asbestos pad. The same process was adopted in the examination of the two systems about to be described.

TABLE I.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$CaCl_2$.	CaO.	$CaCl_2$.	CaO.	Solid phase.
1·025	2·7	0·214	1·0	46·5	$Ca(OH)_2$.
1·048	5·5	0·226	2·0	46·8	
1·056	6·8	0·216	—	—	$Ca(OH)_2 + CaCl_2,3CaO,16H_2O$.
1·067	7·6	0·212	12·7	13·7	$CaCl_2,3CaO,16H_2O$.
1·089	10·2	0·186	13·5	11·2	
1·111	12·5	0·172	15·0	10·7	
1·133	15·2	0·164	16·6	9·8	
1·155	17·4	0·152	18·4	12·4	
1·186	20·0	0·148	20·2	11·8	
1·213	22·8	0·145	21·8	10·7	
1·240	25·6	0·142	23·0	13·4	
1·265	28·0	0·138	24·9	11·9	
1·280	29·7	0·152	26·1	11·1	
1·338	34·9	0·190	31·0	8·3	
1·370	37·6	—	—	—	$CaCl_2,6H_2O$.

D. *The System* $Ca(ClO)_2$–$CaCl_2$–H_2O.—The investigation of this system presented no special difficulty. When calcium hypochlorite was intended to be present as solid phase, it was added in excess to suitable solutions of calcium chloride. It was necessary to have these solutions, particularly when concentrated, free from calcium hydroxide, otherwise the hydroxide, always present in small amount in solid calcium hypochlorite, was converted into basic chloride, and did not pass entirely into solution. A corresponding error in the composition of the residues, which became slightly too rich in calcium chloride, was then produced.

The experimental figures, reproduced in Table II and Fig. 2,

show definitely that no compound of calcium hypochlorite and calcium chloride can be formed in aqueous solution at 0°, and that the composition of the hydrate of the former salt is $Ca(ClO)_2,3H_2O$, and not $Ca(ClO)_2,4H_2O$ as reported by Kingzett and by Orton and Jones (*loc. cit.*). The solubility of this hydrate in water at 0° is 21·8%.

FIG. 2.

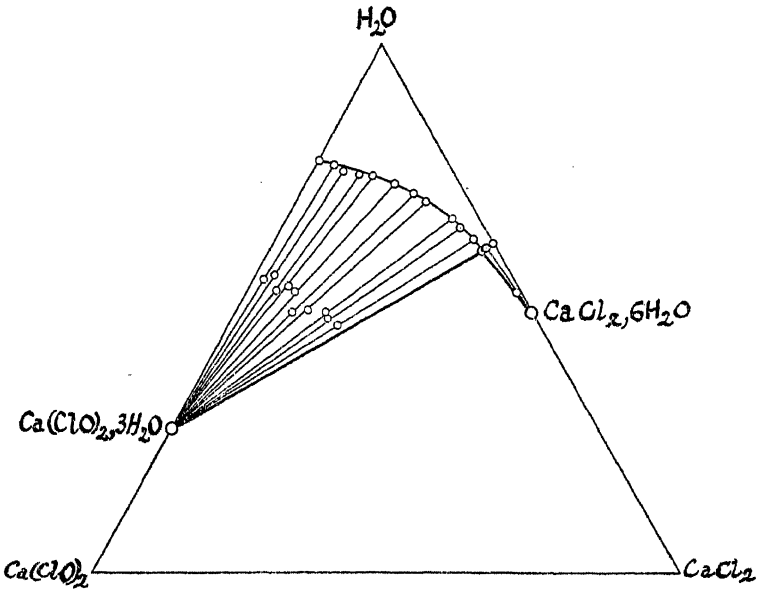


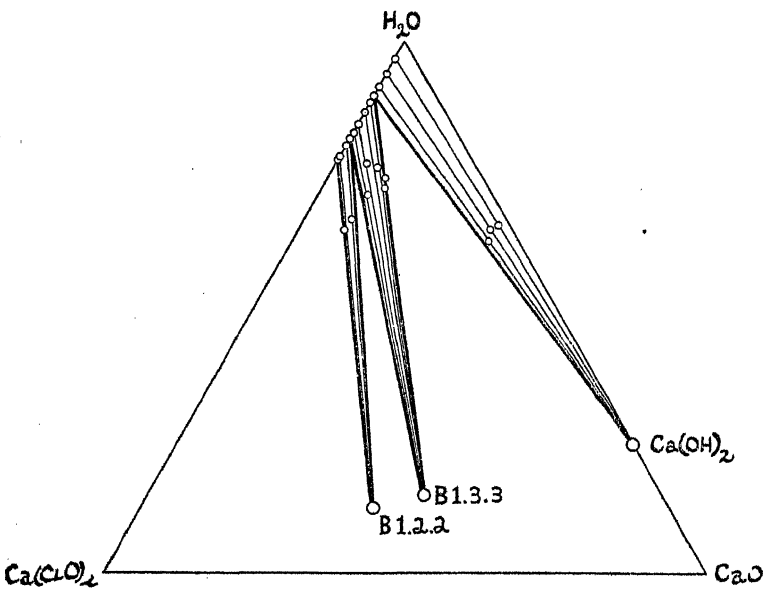
TABLE II.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$Ca(ClO)_2$.	$CaCl_2$.	$Ca(ClO)_2$.	$CaCl_2$.	Solid phase.
1·213	21·8	—	—	—	$Ca(ClO)_2,3H_2O$.
1·220	19·6	3·1	42·5	1·8	
1·228	18·6	5·3	40·2	3·1	
1·234	16·1	8·4	41·5	5·0	
1·238	14·0	10·8	38·9	6·7	
1·255	11·0	15·4	38·5	8·1	
1·270	8·8	19·4	40·8	9·7	
1·285	7·4	22·2	37·8	12·1	
1·322	4·5	28·5	35·0	15·5	
1·333	4·2	30·7	35·2	16·4	
1·366	2·9	34·0	34·1	18·9	
1·388	2·6	36·4	—	—	$Ca(ClO)_2,3H_2O + CaCl_2,6H_2O$.
1·382	1·6	36·9	0·7	46·3	$CaCl_2,6H_2O$.
1·370	—	37·6	—	—	

E. *The System* $Ca(ClO)_2$–CaO–H_2O.—An extended series of measurements was undertaken, the procedure being in all cases

to add solid calcium hypochlorite to milk of lime, and to agitate the resulting complexes for periods varying from 1 to 5 days before analysis. In order to avoid the presence of lumps, freshly burned calcium oxide was slaked in boiling water. Since accurate adjustment of the inital compositions of the complexes was sometimes necessary, the percentage of anhydrous substance in the calcium hypochlorite was determined immediately before use. Two basic salts were found (see Table III and Fig. 3) of formulæ $Ca(ClO)_2,2CaO,2H_2O$ and $Ca(ClO)_2,3CaO,3H_2O$. These are referred to as B 1.2.2 and B 1.3.3, respectively.

FIG. 3.



The salt B 1.2.2 was formed in a few hours from complexes containing from 21·8% to about 16% of calcium hypochlorite, but subsequent investigation showed that its range of stable existence at 0° extends only from 21·8% to 18·0%. Prepared as described above, it was rather voluminous and not visibly crystalline. In consequence, residues containing B 1.2.2 consisted chiefly of solution, although an apparently good filtration had been achieved. Nevertheless, the residue method was quite capable of giving the composition of the solid phase with certainty. The range of stable existence of B 1.2.2 is probably greater above 0°, as it was observed that preparations of B 1.3.3 decomposed on being allowed to warm to room temperature, producing minute crystals. When the rise

TABLE III.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$Ca(ClO)_2$.	CaO.	$Ca(ClO)_2$.	CaO.	Solid phase.
1·030	3·0	0·106	1·85	32·6	$Ca(OH)_2$.
1·053	5·7	0·105	3·5	31·9	
1·077	8·2	0·110	4·8	32·6	
*1·103	11·0	0·114	12·7	31·2	Variable.
*1·122	12·7	—	10·6	19·5	
*1·133	14·0	0·111	13·4	35·0	
1·093	9·9	0·091	15·9	9·8	B 1.3.3.
1·104	11·1	0·093	16·9	10·5	
1·123	13·0	0·093	16·3	7·35	
1·142	15·1	0·077	17·6	5·2	
1·161	16·9	—	20·3	8·3	
1·168	17·8	—	19·2	3·7	
1·171	18·0	—	22·4	6·7	B 1.3.3 + B 1.2.2.
*1·154	16·1	—	16·3	7·4	B 1.2.2.
*1·172	17·7	0·105	21·4	6·8	
1·173	18·2	—	24·0	8·1	
1·189	19·2	0·113	25·3	7·9	
1·188	19·8	0·106	25·0	7·2	
1·203	21·2	0·106	27·3	7·7	
1·213	21·8	—	—	—	$Ca(ClO)_2,3H_2O$.

* Metastable equilibria.

of temperature was slow, these were larger, taking the form of thin plates, 1—2 mm. in diameter, of great transparency and high lustre, entirely free from the greenish-yellow tint of the normal hypochlorite. They were transformed once more into B 1.3.3 on cooling to 0°. An excellent separation of residue from solution was possible, and the subsequent analyses proved conclusively that the crystalline substance was B 1.2.2.

The compound B 1.3.3 was formed after a few hours when calcium hydroxide was agitated at 0° with a solution containing not less than 15% of hypochlorite. It is definitely different in appearance from B 1.2.2, excessively voluminous, and not visibly crystalline. In consequence, the compositions of solutions and corresponding residues were quite close together. A complex consisting of 50 c.c. of the above solution with about 1 g. of calcium hydroxide became of the consistency of cream, and larger amounts of calcium hydroxide produced a semi-solid mass—a fact which suggests that the basic salt may be highly hydrated; but all the evidence (see Fig. 3) is against this supposition. Over a range of solutions containing from 18·0% to 9·9% of calcium hypochlorite, the tie-lines converge fairly well upon the point representing B 1.3.3. They converge better on a point slightly to the right of this along a line joining the points representing B 1.3.3 and calcium hydroxide. This would indicate a basic salt of approximate composition B 2.7.7,

but the discrepancy may be due to experimental error or to the peculiarities of the system itself.

Introduction of a suspension of B 1.3.3. into preparations in which B 1.2.2 had been formed as solid phase revealed the metastable existence of the latter in contact with solutions containing from 18·0% to about 16% of hypochlorite, the change of solid phase occurring after a few hours' rotation. Owing to the relatively small quantities of calcium hydroxide which could be used, and the correspondingly small amounts of hypochlorite taken up in forming B 1.2.2 or B 1.3.3, it was not easy to obtain a residue containing both basic salts. This was finally produced by inoculating with B 1.3.3 a series of preparations which differed only very slightly from one another in initial composition, and in which B 1.2.2 had already been formed. The difference in appearance of the two basic salts confirmed the analytical results.

The equilibrium of B 1.3.3 and calcium hydroxide with solution could not be determined satisfactorily in spite of many attempts. The separation of B 1.3.3 did not always occur spontaneously when calcium hydroxide was agitated with solutions containing less than about 14% of calcium hypochlorite. Inoculation from another preparation caused it to separate, less and less readily, however, as the concentration of the solution fell. Below a concentration of 10% the appearance of the suspended solid and of the residues was entirely that of calcium hydroxide, even after inoculation and subsequent rotation for several days, but analysis revealed a small proportion of hypochlorite in the solid phase. The best available approximation to the conditions of the equilibrium in question was obtained as follows. About 40 c.c. of a solution containing some 13% of calcium hypochlorite in contact with 2·5 g. of calcium hydroxide were seeded with B 1.3.3 and rotated for several days. A large quantity of B 1.3.3 separated, but, owing probably to its slow formation, did not make the preparation unmanageable. The solution contained 9·9% hypochlorite, and the residue was practically free from hydroxide. Similar treatment of preparations in which the initial concentrations of the solutions varied from 12% to 10% yielded final solutions more concentrated than the above and residues of B 1.3.3 and calcium hydroxide. Reproducible results could not be obtained, and after a number of experiments the figure 9·9% was taken as a provisional lower limit to the range of stable existence of B 1.3.3 in contact with solution.

The concentration of calcium hydroxide in the solutions was small and its variation smaller, furnishing no guide to the establishment of equilibrium. In some cases, it was not determined.

When agitated with solutions containing from 14% to 10% of calcium hypochlorite, calcium hydroxide took up varying small quantities of hypochlorite, which increased with both the concentration of the solution and the time of agitation. Below 10%, the quantity was negligible. The appearance of the solid phase and residues was that of calcium hydroxide. This effect points to adsorption, mixed crystal formation, or production of some basic salt in variable amounts; but no decision between these possibilities could be made. Some of the analytical results are included in Table III, marked with an asterisk to indicate that they represent metastable conditions. Only equilibria believed to be stable are shown in Fig. 3.

Of the basic salts reported by the Chemische Fabrik Griesheim-Elektron (*loc. cit.*), only two (B 1.2.2 and B 1.3.3) have been found to exist at 0° in contact with solutions containing hypochlorite and hydroxide. There is no definite evidence at this temperature of any other basic salt.

Conclusions.

Although equilibria in the appropriate quaternary system have not been investigated, it is possible to discuss at the present stage the probable composition of bleaching powder. A fresh sample, prepared by chlorinating nearly dry calcium hydroxide and containing about 35% of available chlorine, is roughly of the composition $2Ca(ClO)_2 + 2CaCl_2 + 3Ca(OH)_2 + 4H_2O$. No compound of calcium hypochlorite and chloride exists at 0°, and the same is probably true at higher temperatures, as indicated by the method given for the preparation of the former salt. If present separately, the hypochlorite and chloride cannot be wholly in the form of trihydrate and hexahydrate, respectively, because the amount of water present is too small. Lower degrees of hydration, at least of the calcium chloride, are possible. Further, in ordinary good bleaching powder, the proportion of calcium hydroxide is too small to convert completely either the hypochlorite or the chloride present into any of the known basic salts, except $CaCl_2,CaO,2H_2O$. The extent to which these substances are present in dry bleaching powder prepared in the usual way is necessarily problematical, and is further limited in the case of $CaCl_2,3CaO,16H_2O$ by the amount of water available. The equilibrium distribution of the water and calcium hydroxide present, and the possibility of formation of a basic double salt cannot be discussed on the basis of the data at present available, but it appears likely that, in a solid preparation, basic salt formation, if it occurs at all, would be slow, and that fresh bleaching powder is therefore simply a mixture of calcium hydroxide with more or less hydrated hypochlorite and chloride.

Summary.

1. A method was developed for the isolation of relatively pure calcium hypochlorite.

2. The ternary systems $CaCl_2$–CaO–H_2O, $Ca(ClO)_2$–$CaCl_2$–H_2O, and $Ca(ClO)_2$–CaO–H_2O have been investigated at 0°.

3. Basic salts $CaCl_2,3CaO,16H_2O$; $Ca(ClO)_2,CaO,2H_2O$; and $Ca(ClO)_2,3CaO,3H_2O$ were identified.

4. No double salt was formed by calcium hypochlorite and calcium chloride.

5. The probable composition of bleaching powder has been discussed in the light of these results.

It is proposed to extend this investigation, and to attempt the isolation of the hypochlorites of metals other than calcium.

THE UNIVERSITY OF QUEENSLAND,
BRISBANE. [*Received, June 22nd,* 1927.]

CCCLIX.—*Some Effects of the Uneven Distribution of Current Density over an Electrode.*

By ERNEST SYDNEY HEDGES.

IN the ordinary course of electrolysis, the current density is not evenly distributed over a rectangular electrode, but tends to concentrate at the corners and edges. (Possibly, this is related to the well-known tendency of an electric charge to escape from a point.) Thus, whenever film formation takes place at such an electrode, the film first forms at the lowest part of the electrode and travels up the metal in the form of a U of diminishing concavity. This is not due to a concentration gradient in the solution, for the phenomenon occurs however vigorously the liquid is stirred, and is independent of the direction of flow of liquid over the electrode. For the same reason, the inside of an anode (*i.e.*, the side facing the cathode) is more readily attacked than the outside. At a cathode, more metal is deposited on the inside than on the outer side, and the deposit is thicker at the corners and edges.

In experiments with the easily passivated metals, some curious effects were observed through this behaviour. Anodes of iron were often found to be passive on the inside and active on the outside, where no oxygen was evolved; or, at somewhat higher *C.D.*'s, the lower portion of the outside of the electrode became passive, leaving the upper portion active, with the characteristic U-shaped boundary of separation. In certain cases, a small active

area was left near the liquid line, where rapid corrosion took place (compare Evans, J., 1927, 1035; Hedges, J., 1926, 831). It may be necessary to consider this factor in the type of liquid-line corrosion which is characterised by the presence of passivating media. In other cases, the main electrode remained active, whilst just the corners and edges of the electrode became passive. The most striking effects were observed with anodes of cobalt, which readily become passive, with evolution of oxygen, in moderately concentrated solutions of sulphuric acid. In 50% (by vol.) sulphuric acid cobalt dissolves at low *C.D.*'s as a pink, cobaltous ion, but at higher *C.D.*'s it goes into solution as a green cobaltic compound. It was frequently observed that the inside of the electrode was dissolving to give a green solution, whilst the outside dissolved simultaneously to form a red solution.

An interesting conclusion may be drawn from these observations in connexion with Adler's theory (*Z. physikal. Chem.*, 1912, **80**, 385) of the cause of the periodic anodic dissolution of passive metals, according to which the periodic phenomenon is to be traced to alternations of polarity in local elements composing the electrode. In the experiments described above, periodic phenomena were observed, but they did not consist of an alternation of the active and passive regions. The phenomena did not differ in any respect from those observed at higher *C.D.*'s, when the whole surface of the electrode became alternately active and passive. Moreover, electrodes have been observed which, although clearly differentiated into active and passive zones, did not dissolve periodically.

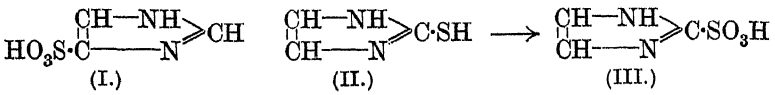
BEDFORD COLLEGE (UNIVERSITY OF LONDON),
REGENT'S PARK, N.W. 1. [*Received, October 7th*, 1927.]

CCCLX.—*The Sulphonation of Glyoxalines. Part III.*

By GEORGE REGINALD BARNES AND FRANK LEE PYMAN.

SULPHONATION of glyoxalines leads to a monosulphonic acid, which was assumed to be glyoxaline-4(5)-sulphonic acid (I) (Pyman and Ravald, J., 1920, **117**, 1429), but attempts to prove the orientation of the sulpho-group failed (Forsyth, Moore, and Pyman, J., 1924, **125**, 919). Recently, Balaban and King (this vol., p. 1858) have shown that 2-thiol-4(5)-methylglyoxaline can be oxidised to 4(5)-methylglyoxaline-2-sulphonic acid by means of hydrogen peroxide, and with the consent of these authors we have oxidised 2-thiolglyoxaline (II) to *glyoxaline-2-sulphonic acid* (III) by their method. It proves to be different from the sulphonation product of glyoxaline,

which is thus shown to be glyoxaline-4(5)-sulphonic acid, as previously supposed.



(I.) (II.) (III.)

4(5)-Methylglyoxaline has now been sulphonated, and yields a sulphonic acid which must be 4(5)-*methylglyoxaline*-5(4)-*sulphonic acid* (IV), since it is not identical with Balaban and King's 4(5)-methylglyoxaline-2-sulphonic acid (V).



(IV.) (V.)

It resembles glyoxaline-4(5)-sulphonic acid and 2-methylglyoxaline-4(5)-sulphonic acid in being readily decomposed by cold bromine water and in failing to yield an acid chloride on treatment with phosphorus pentachloride. Like glyoxaline-4(5)-sulphonic acid, it is hydrolysed almost quantitatively by heating for 3 hours at 170° with concentrated hydrochloric acid, but glyoxaline-2-sulphonic acid is hydrolysed only to the extent of 12% under these conditions. It may be noted that all the many sulphonation and nitration products of glyoxalines which have been oriented hitherto contain the sulpho- or nitro-group in the 4- or 5-position, and there is no evidence at present that glyoxalines can be sulphonated or nitrated in the 2-position.

Experimental.

Glyoxaline-2-sulphonic Acid (III).—2-Thiolglyoxaline (3·21 g.) was added to Merck's perhydrol (10·92 g.) diluted with water (21·8 c.c.) at — 5° to 0°. The solution was basified with sodium hydroxide, kept at 0° for 12 hours, and acidified to Congo-red with hydrochloric acid. When the solution was concentrated, *glyoxaline-2-sulphonic acid* (2·46 g.; yield 46·2%) separated. The mother-liquor was basified with potassium carbonate, evaporated to dryness, and extracted with alcohol. This extract gave with picric acid glyoxaline picrate (0·8 g.; yield 8·4%).

Glyoxaline-2-sulphonic acid crystallises from water in colourless prisms containing $1H_2O$, which is lost in a vacuum over sulphuric acid. The dried acid softens and darkens from 285° and melts at about 303° (corr.), whilst a mixture of this acid with the monosulphonic acid formed by the sulphonation of glyoxaline—glyoxaline-4(5)-sulphonic acid, m. p. 307°—melted at 272—275°. (The latter crystallises from water in anhydrous cubes; Pyman and Ravald, *loc. cit.*) (Found: loss in a vacuum over H_2SO_4, 11·0, 11·1.

$C_3H_4O_3N_2S,H_2O$ requires H_2O, 10·8%. Found in dried acid: C, 24·3; H, 3·1; S, 21·7. $C_3H_4O_3N_2S$ requires C, 24·2; H, 2·7; S, 21·6%).

Glyoxaline-2-sulphonic acid is soluble in about 8 parts of cold water, more readily soluble in hot water, but insoluble in absolute alcohol.

The *barium* salt crystallises from water in feathery needles containing $2H_2O$, and is soluble in about 3 parts of cold water, more readily soluble in hot water, but insoluble in alcohol [Found: loss at 120°, 7·2. $(C_3H_3O_3N_2S)_2Ba,2H_2O$ requires H_2O, 7·7%. Found in dried salt: Ba, 31·3, 31·4. $(C_3H_3O_3N_2S)_2Ba$ requires Ba, 31·8%]. [Barium glyoxaline-4(5)-sulphonate crystallises from water in anhydrous octahedra; Pyman and Ravald, *loc. cit.*].

Hydrolysis. Glyoxaline-2-sulphonic acid (0·83 g.) and concentrated hydrochloric acid (8·3 c.c.) were heated for 3 hours at 170°, and the product was mixed with aqueous barium chloride; barium sulphate was then precipitated in quantity (0·14 g.) corresponding to the hydrolysis of 12% of the acid. After removal of the excess of barium by means of sulphuric acid, and of hydrochloric acid by means of silver hydroxide, 0·45 g. (54%) of glyoxaline-2-sulphonic acid was recovered unchanged, whilst the mother-liquor gave with picric acid glyoxaline picrate (0·1 g.; yield 6·7%). This melted at 205°, and did not depress the m. p. of an authentic specimen of glyoxaline picrate.

Sulphonation of 4(5)-*Methylglyoxaline.*—The well-dried and finely powdered sulphate from 16·76 g. of 4(5)-methylglyoxaline was added to 60—70% oleum (67·0 g.) at 0°, and the mixture heated for 6 hours at 160°. The product was diluted with water, and sulphuric acid removed by means of barium hydroxide, excess of the latter being removed by carbon dioxide. The filtered solution was evaporated to dryness, and the residue was extracted with chloroform, which removed no unchanged base, and dried at 120°; 43·44 g. of crude barium salt containing 29·2% Ba were then obtained. These figures correspond to a yield of 90·5% of barium 4(5)-methylglyoxaline-5(4)-sulphonate, but when the salt was treated with the calculated quantity of sulphuric acid pure 4(5)-methylglyoxaline-5(4)-sulphonic acid was obtained in only 60% yield, and was accompanied by small quantities of a by-product more sparingly soluble in water, which was not obtained in a pure state.

4(5)-*Methylglyoxaline*-5(4)-*sulphonic acid* (IV) crystallises from water in colourless, hexagonal plates containing $1H_2O$, which is lost at 100°. The dried acid melts at 278° (corr.) after sintering a few degrees lower. A mixture of this acid with a specimen of 4(5)-methylglyoxaline-2-sulphonic acid (m. p. 280°), for which we

are indebted to Dr. King, melted at 235—240° (Found in air-dried acid: loss at 100°, 9·8, 10·0. $C_4H_6O_3N_2S,H_2O$ requires H_2O, 10·0%. Found in dried acid: C, 29·5; H, 4·1; N, 17·4; S, 20·2. $C_4H_6O_3N_2S$ requires C, 29·6; H, 3·7; N, 17·4; S, 19·8%). The acid is soluble in about 4 parts of cold water, more readily soluble in hot water, but insoluble in alcohol or ether.

The *sodium* salt crystallises from water in long, silky needles, containing $3H_2O$, and is soluble in about 2·5 parts of cold water, but insoluble in alcohol (Found in air-dried salt: H_2O, 21·7, 21·6; Na, 9·5, 9·6. $C_4H_5O_3N_2SNa,3H_2O$ requires H_2O, 22·7; Na, 9·7%). The *ammonium* salt crystallises from water in anhydrous prisms which are soluble in about 4 parts of cold water but insoluble in alcohol (Found: N, 23·3. $C_4H_9O_3N_2S$ requires N, 23·4%). The *barium* salt crystallises from 50% aqueous alcohol in long, opaque needles, containing $3H_2O$. It is soluble in 2 parts of cold water, but insoluble in alcohol [Found in air-dried salt: loss at 120°, 10·2, 10·4. $(C_4H_5O_3N_2S)_2Ba,3H_2O$ requires H_2O, 10·5%. Found in dried salt: Ba, 29·3, 29·5. $(C_4H_5O_3N_2S)_2Ba$ requires Ba, 29·8%].

Hydrolysis. 4(5)-Methylglyoxaline-5(4)-sulphonic acid (0·9 g.) was heated with concentrated hydrochloric acid (10 c.c.) for 3 hours at 170°. The product was mixed with aqueous barium chloride and gave 1·166 g. of barium sulphate corresponding to the hydrolysis of 99·8% of the acid. The filtrate was basified with sodium carbonate, filtered from barium carbonate, and evaporated to dryness. On extraction of the residue with chloroform an oil was obtained which gave with alcoholic picric acid 4(5)-methylglyoxaline picrate (0·89 g.; yield 57%; m. p. 159—160°, alone or mixed with an authentic specimen).

Bromination. To the hydrated sulphonic acid (9·62 g.) in cold water (100 c.c.), bromine (1 mol.; 2·7 c.c.) was added, and the colour of this was immediately discharged. On concentrating the solution and, on occasions, adding alcohol, various crops of crystals were obtained from which the unchanged acid (5·22 g.) and ammonium bromide (1·5 g.) were isolated. The final mother-liquor contained 1·03 g. of sulphuric acid.

Anhydrous 4(5)-methylglyoxaline-5(4)-sulphonic acid did not appear to react with phosphorus pentachloride at 160°.

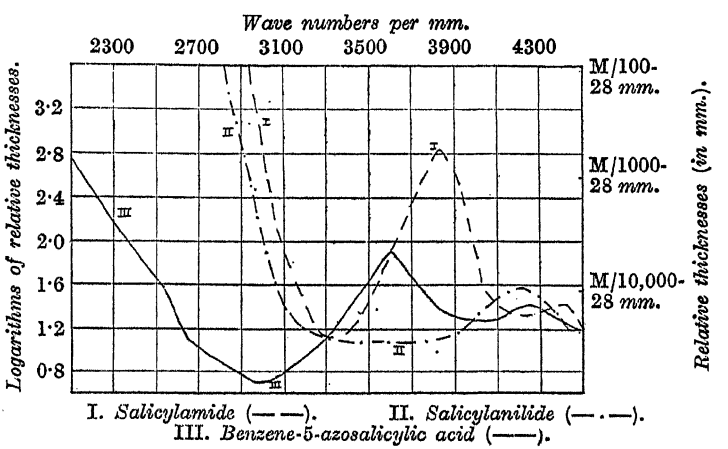
MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, October 5th*, 1927.]

CCCLXI.—*The Absorption Spectra of Various Alkaloids and their Salicylates and of other Derivatives of Salicylic Acid.*

By JOHN EDWARD PURVIS.

IN previous communications (J., 1925, **127**, 2771; 1926, 775; this vol., p. 780), the author has discussed the influence of the basic and acidic constituents of various salts on their absorption spectra. This communication is to describe the results of further investigations on the spectra of various alkaloids and their salicylates, and of other compounds derived from salicylic acid. The substances were dissolved in pure ethyl alcohol and a condensed cadmium spark was the source of radiant energy.

FIG. 1.



I. *Salicylamide* (— —). II. *Salicylanilide* (— · —).
III. *Benzene-5-azosalicylic acid* (——).

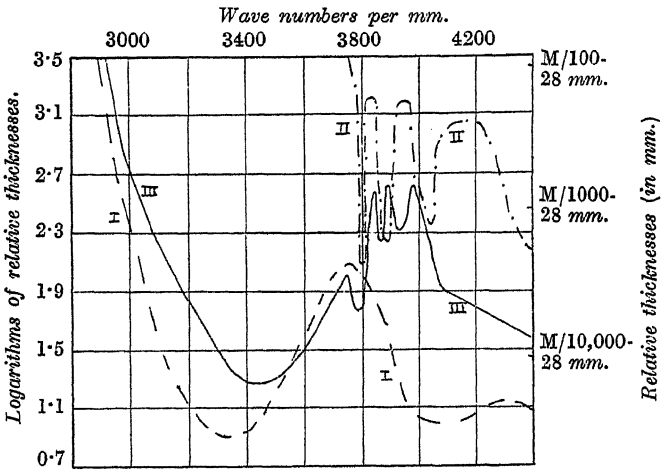
Salicylamide (Fig. 1, I) shows two bands. They are not unlike those of salicylic acid, but the more refrangible one is not quite so well marked as that of the acid. Hartley and Hedley (J., 1907, **91**, 319) found that the bands of benzamide and benzoic acid were comparable, except that the benzamide band was not so wide as that of the acid.

Salicylanilide has one large band (Fig. 1, II). Aniline itself has two large bands, namely, between $1/\lambda$ 3508 and $1/\lambda$ 3648 and between $1/\lambda$ 4165 and $1/\lambda$ 4309, as described by Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, 257) and by Baly and his colleagues (J., 1905, **87**, 1332; 1915, **107**, 1058). In salicylanilide, therefore, the two bands of aniline and the two bands of salicylic acid have been fused into one large band which covers the positions formerly

occupied by the bands of aniline and salicylic acid. These results are comparable with those obtained with benzanilide, where the bands of benzene and of aniline are replaced by one large band (Crymble, Stewart, Wright, and Glendinning, J., 1911, 99, 451).

Benzene-5-azosalicylic acid shows two bands (Fig. 1, III). The absorption of the less refrangible and very wide one extends into the coloured regions, the group $C_6H_5\cdot N{:}N\cdot$ probably accounting for the colour. The more refrangible band is weaker than the corresponding band of salicylic acid and almost disappears.

FIG. 2.



I. o-*Salicoyloxybenzoic acid* (— —). II. *Atropine* (— . —). III. *Atropine salicylate* (——).

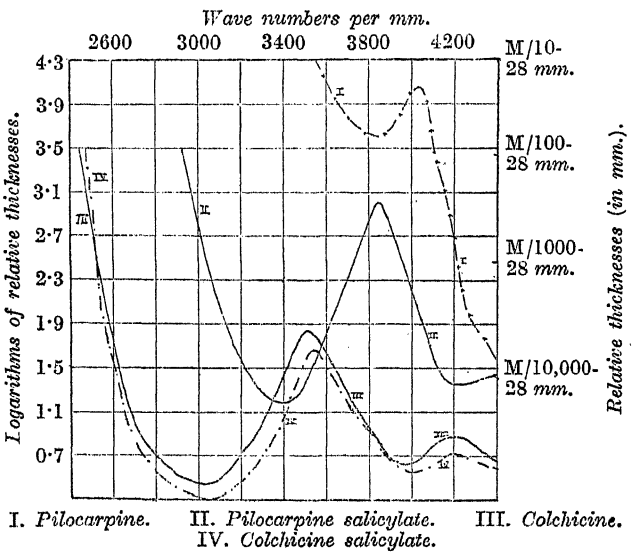
o-*Salicoyloxybenzoic acid* (Fig. 2, I) shows two bands not unlike those of salicylic acid in their general form, but shifted more towards the red end. It has been noticed (*loc. cit.*) that when the hydrogen of the hydroxyl group of salicylic acid is replaced by an acetyl group, as in *o*-acetoxybenzoic acid and other similar compounds, a striking change is produced and the absorption phenomena are not unlike those of benzoic acid. In *o*-salicoyloxybenzoic acid there is no such change, so that the presence of hydrogen of the hydroxyl group of $OH\cdot C_6H_4\cdot CO\cdot$ combined with the other group $-O\cdot C_6H_4\cdot CO_2H$ to produce the acid $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$ enables the compound to retain the characteristic absorption of salicylic acid itself.

Atropine and Atropine Salicylate.—Dobbie and Fox (J., 1913, **103**, 1193) describe two bands of atropine at about $1/\lambda$ 3770 and $1/\lambda$ 3880. Gompel and Henri (*Compt. rend.*, 1913, **156**, 1541) found a third, weaker, band at $1/\lambda$ 4020. The author has repeated

these experiments and can confirm the presence of three bands (Fig. 2, II).

The curve of atropine salicylate (Fig. 2, III) exhibits a large band like that of salicylic acid, but not quite so strong. Besides that, there are three weak bands on the more refrangible side of this large band, and these are comparable with the three bands of atropine, but a little weaker. The more refrangible band of the acid is represented in the salt by a rapid extension of the rays between about $1/\lambda$ 4100 and $1/\lambda$ 4450. It is obvious, therefore, that the bands of both base and acid are still well marked in the

FIG. 3.



salt, the chief differences being the weaker appearances of the bands of the latter. A sharper differentiation of the separate bands of the basic and acidic parts of the salt could only be made by an instrument of much greater dispersion. This remark applies to the following observations of other alkaloids and their salts.

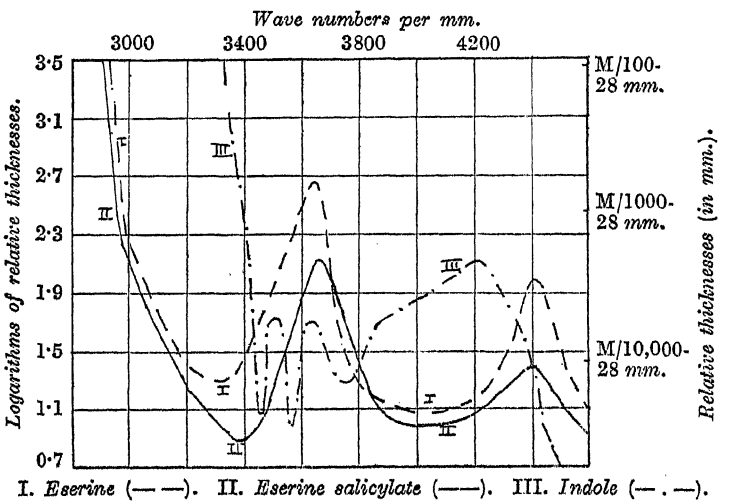
Pilocarpine and Pilocarpine Salicylate.—In Jowett's investigation of pilocarpine (J., 1903, **83**, 438), Dobbie describes a weak band of pilocarpine nitrate at about $1/\lambda$ 3350. The author has repeated the observations with an alcoholic solution of the base itself and finds a weak band at about $1/\lambda$ 3800 (Fig. 3, I).

Pilocarpine salicylate shows two bands of salicylic acid (Fig. 3, II). As the thickness of the solution increases, the less refrangible band of the salt appears to be slightly wider than that of the acid; and

this is probably caused by the latter impinging on the weak band of the base and covering it up; the absorptive power of the base only becomes visible as the thickness of the solution increases. A saturated solution of pilocarpine salicylate was also examined, but there was no appearance of a separate band of pilocarpine, showing that the bands of the acidic constituent covered up that of the basic part. The more refrangible band of the salt is not so well marked as that of the acid itself.

Colchicine and Colchicine Salicylate.—The curves show (Fig. 3, III and IV) that each substance has two bands. The less refrangible band of the salt is wider on the more refrangible side than that of

FIG. 4.



I. *Eserine* (— —). II. *Eserine salicylate* (——). III. *Indole* (— . —).

the base, and the more refrangible band of the base is stronger than the more refrangible one of the salt. These differences are probably again caused by the overlapping of the separate bands of the basic and acidic constituents. A greater dispersion would be necessary to separate these bands more sharply. The general shift of the absorption towards the red end explains the slight yellow colour of both these substances.

Eserine (Physostigmine) and Eserine Salicylate.—The absorption curves (Fig. 4, I and II) show that each substance has two large bands, and, as in colchicine and its salicylate, the differences are the result of the bands of the acid and basic constituents partly overlapping each other. It was suggested by Stedman and Barger and experimentally confirmed by Späth and Brunner (*Ber.*, 1925, **58**, 518) that physostigmine is a substituted indoline. The author

has investigated the absorption of indole and the curve is compared with that of eserine (Fig. 4, III). This exhibits several bands at 1/λ 3460, 1/λ 3560, and a weaker wider one at 1/λ 3750. There is also a rapid extension of the line of absorption to about 1/λ 4200, and this probably indicates other weaker bands. All the bands of indole disappear in eserine.

These results are to be compared with those described in the previous investigations (*loc. cit.*). In camphor salicylate, for example, the weak band of camphor at 1/λ 3480 would appear to be covered up by the less refrangible strong band of salicylic acid, which widens out with increased thickness of the solution, to 1/λ 3600. Camphor salicylate has again been studied in *M*/10-solutions, and these are stronger than those of the earlier observations, and through thicknesses of from 2 mm. to 28 mm. No camphor band appeared, whereas in camphor itself the band is perfectly clear in such strengths. Similar explanations account for the differences in theobromine and caffeine and their salicylates (*loc. cit.*). In the salicylates of phenazone and quinine (*loc. cit.*), the differences in the absorption are more clearly marked because the specific bands of the bases themselves are fairly strong, and they are not hidden by the bands of the acid nuclei.

The specific absorptive capacity of these compounds, therefore, appears to depend upon the more or less intimate chemical combination of the various centres, as well as upon their chemical type. Where the chemical combination is not so close, as in the salicylates of the alkaloids, both the basic and the acid nuclei largely retain their own specific absorption. On the other hand, where there is a closer chemical combination of the absorbing centres, as, for example, in salicylanilide or benzene-5-azosalicylic acid, the specific absorption of each centre is not so sharply defined. Each centre is influenced by the other centres to a much larger extent than in the salicylates of the alkaloids and other organic bases.

PUBLIC HEALTH CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, July 1st*, 1927.]

CCCLXII.—*Organic Derivatives of Silicon. Part XXXIII. An Amorphous Variety of Octaphenylcyclosilicotetrane.*

By FREDERIC STANLEY KIPPING.

THE glue-like, readily soluble product (E) of the action of sodium on diphenylsilicon dichloride in toluene solution is so strikingly different in physical properties from the four very sparingly soluble

silicohydrocarbons $[SiPh_2]_n$ (A, B, C, and D) by which it is accompanied (Kipping and Sands, J., 1921, **119**, 830) that it could hardly fail to arouse interest; its investigation, continued intermittently since 1921, has led to the conclusion that it consists mainly of an amorphous form of octaphenyl*cyclo*silicotetrane (B), the crystalline variety of which does not melt at 400° and is practically insoluble in cold acetone.

The acetone solution of (E) (*loc. cit.*, p. 836), kept in a closed vessel, continues to deposit crystals, but in gradually diminishing quantities, over periods of more than two years; these deposits consist of octaphenyl*cyclo*silicotetrane (B), but contain, as a rule, a very small proportion of the compound (C) (Kipping, J., 1924, **125**, 2291); octaphenylsilicotetrane (A), which is much more soluble than (C), but much less soluble than (B), in ordinary media, has never been detected. It seems, therefore, that (E) is partly and very slowly transformed into (B), since ordinary supersaturation could hardly continue so long. When the acetone solution is systematically fractionally precipitated with alcohol, a very small proportion of (B) and sometimes traces of (C) are found after each extended set of operations, and this separation or formation of insoluble matter seems to continue almost indefinitely; most of the original preparation, however, is merely resolved into a series of fractions, all miscible with acetone, the more sparingly soluble of which consist of an easily fusible resinous material of the composition $[SiPh_2]_n$, hereafter referred to as (E_1). The more soluble fractions are glue-like or oily, and contain combined oxygen, the origin of which was ultimately traced to the presence of phenoxy- and ethoxy-compounds in the diphenylsilicon dichloride (compare Kipping and Murray, this vol., p. 2734). This discovery and the difficulty of settling the nature of (E_1) made it advisable to hold back the results of its investigation until there was no doubt of its formation from the dichloride.

Even after prolonged fractionation from many different solvents, (E_1) yields no crystalline compound, other than a little (B) and traces of (C); it merely affords a series of graded fractions. Cryoscopic determinations in benzene solution give multiples of $SiPh_2$ ranging from about 7 to 9, and the high molecular complexity of the material is also proved by its non-volatility at high temperatures in a vacuum (p. 2725).

In chemical behaviour, (E_1) resembles octaphenyl*cyclo*silicotetrane (B) and is quite different from the reactive, open-chain isomeride (A); the fact that it does not combine with iodine seems to indicate, but does not prove [compare behaviour of (D), J., 1924, **125**, 2296], that it consists entirely of closed-chain molecules. It

is oxidised by nitric acid, giving a small proportion of the rhomboidal oxide, $Si_4Ph_8O_2$ (J., 1921, **119**, 844), but practically the whole of it seems to be converted into diphenylsilicanediol and condensation products of the latter. It is decomposed by piperidine and aqueous alkali, giving hydrogen and diphenylsilicanediol (or condensation products). The observed hydrogen values (Kipping and Sands, *loc. cit.*, p. 848) are a little lower than that required for $SiPh_2 + 2H_2O = SiPh_2(OH)_2 + H_2$, probably owing to incomplete hydrolysis; the examination of the products (p. 2727) seems to prove, however, that the preparations do not contain any $SiPh_3$-groups, but consist entirely of molecules $[SiPh_2]_n$.

Now when the physical properties of (E_1) are compared with those of octaphenyl*cyclo*silicotetrane (B) and those of (C), which is possibly $[SiPh_2]_6$ or $[SiPh_2]_8$—leaving out of consideration those of the open-chain compounds (A) and (D)—the contrast is so striking that even if (E_1) were regarded as a mixture of several cyclic compounds $[SiPh_2]_n$, the latter could hardly be present as free molecules, capable of forming sparingly soluble crystalline structures of high melting point, like those of (B) and (C). It is therefore suggested that (E_1) consists of molecules of octaphenyl*cyclo*silicotetrane (B) which have got so entangled with one another during their formation that they are inseparable, or nearly so, by physical means at moderate temperatures. It is not assumed that the cyclic structures are joined together like the links of a chain, but that the molecules of (B) are held together by the interlocking of their phenyl groups, forming aggregates of irregular shape, which do not themselves pack into crystals and hinder the orderly arrangement of the whole; if some of these molecules were comparatively loosely attached, and the proportion of irregular aggregates was diminished, a slow deposition of ordinary crystals of (B) from solutions of (E_1) might be expected to take place to a certain extent, as actually occurs. It is possible that octaphenyl*cyclo*silicotetrane and its higher analogues might assume configurations in which the silicon atoms do not all lie in one plane, and that such configurations might be rendered stable by the steric effects of their phenyl groups. Such assumptions, however, would not account adequately for the properties of (E_1), which seems to be a complex mixture of molecules, incapable of crystallisation.

The view that (E_1) is merely a physically different form of (B) is borne out by the following: In one experiment, when (E) was heated under 5—0 mm., small quantities of oily "distillate," apparently decomposition products, were collected as the temperature of the liquid rose from about 300° to 400° and at the same time a very considerable proportion of crystalline matter separated

from the residue, and did not all redissolve; this crystalline deposit consisted of octaphenyl*cyclo*silicotetrane (B) with a small proportion of octaphenylsilicotetrane (A). As it was hardly possible that so large a proportion of free (B) molecules could have been present in the crude (E), it must be concluded that these molecules had been set free by the action of heat.

Unfortunately, attempts to repeat this conversion of (E_1) into (B) have been unsuccessful, but the reverse operation is easily accomplished. When pure (B) is very rapidly heated above 400° until it is partly melted, and then immediately cooled, the glue-like melted portion is very readily soluble in cold acetone; the solution begins to deposit crystals of (B) after a variable interval and continues to do so during several days or weeks; it then gives with alcohol a flocculent precipitate, $[SiPh_2]_n$, melting indefinitely below 150°, and having a molecular weight of about 1500.

These results, the chemical similarity of (E_1) and (B), and all other facts seem to be best accounted for by the assumption that these two substances are physically different forms of octaphenyl-*cyclo*silicotetrane.

The distillate referred to above, and a similar product from other samples of (E), consisted mainly of an oil which gave triphenylsilicol on oxidation, or, with evolution of hydrogen, on treatment with acetone and alkali; from these facts, it would appear that this oil contained triphenylsilicyl, pentaphenylsilicoethyl, or heptaphenylsilicopropyl. It is only formed from (E) very slowly and at high temperatures, but it is clear that the decomposition of the $[SiPh_2]_n$ molecules is accompanied by a transference of phenyl groups from one silicon atom to another.

Experimental.

The crystalline deposit which is formed when an acetone or ethereal solution of (E) is kept in a closed vessel does not redissolve when the supernatant solution is warmed; separated by filtration and treated with cold benzene, it often leaves a very small proportion of a residue which can be identified as (C) by crystallisation from benzene, etc. (compare J., 1924, **125**, 2294). The main portion of the deposit, soluble in cold benzene, was identified as octaphenyl*cyclo*silicotetrane (B) by direct comparison; it did not decolorise a very dilute benzene solution of iodine and was therefore free from octaphenylsilicotetrane (A).

As the formation of deposits in acetone solutions of (E) might conceivably be due to the action of alkali from the glass vessels, an acetone solution which had been kept some 3 months was filtered and acidified with a drop of hydrochloric acid; the solution (in a

closed vessel, gave in the course of 6 months a deposit of (B), and the flask became coated with a very thin layer of some material insoluble in boiling benzene and other solvents, which could be detached in transparent, elastic films. Similar gelatinous films are often formed on the beakers used in fractionating (E) with acetone and alcohol; they char at a very high temperature but without melting and appear to be unchanged when boiled with acetone and potash. This material may be already contained in (E) and if so may be partly accountable for the low hydrogen values of (E_1), or it may be a very complex condensation product of diphenylsilicanediol (which will be described in a future paper), produced by the hydrolysis of (E_1). Crude (E) does not react appreciably with iodine, but it reduces silver nitrate in acetone solution very distinctly.

Separation of Silicohydrocarbons (E_1).—Treated with alcohol, the acetone solution of (E) gives at first a white, plastic precipitate which can be pulled out into long, silk-like threads; the latter change into a very brittle solid when the solvents evaporate. By systematic fractional precipitation in this way, or with water, continued until each of the original fractions (say 8) has been redissolved and reprecipitated several times, the most sparingly soluble portion, now precipitated in a flocculent form, if again treated with cold acetone, usually gives a very small separation of (B) with traces of (C). Another systematic series of operations with the whole set of fractions, starting from the most soluble portion, yields a similar result, and it seems that this very sparingly soluble matter is being continually produced.

Many different preparations of the less soluble fractions (but miscible with acetone) have been analysed; most of them retained solvent very tenaciously and lost in weight during more than 30 days in a vacuum * (Found: Si, 15·3, 15·7, 15·5, 15·6, 15·4, 15·6; C, 77·6, 78·2, 77·9, 78·3; H, 5·9, 5·8, 5·9, 5·8; *M*, cryoscopic in benzene, 1558, 1395, 1456, 1225, 1410; hydrogen values, 110, 108, 113, 116. $SiPh_2$ requires Si, 15·5; C, 79·0; H, 5·5%; *M*, 182; hydrogen value, 122) (compare J., 1921, **119**, 848).

The somewhat low combustion results are partly due to the difficulty of burning the last traces of carbon in the silica residue;

* The best way of obtaining a sample ready for analysis is to dissolve it (2—3 g.) in a very little dry ether in a 300 c.c. beaker, evaporate the solvent on the water-bath to a "glue," and then, while the "glue" is still warm, evaporate the rest of the solvent quickly under reduced pressure; the residue froths and fills the beaker with a white foam, which after 10—15 minutes becomes very brittle and can be easily broken up. Even such preparations do not become constant in weight in less than 3 to 5 days in a vacuum; to the unaided eye they appear to be beautifully crystalline.

the silicon determinations are trustworthy, since the residue obtained on ignition with sulphuric acid containing a little nitric acid is colourless.* The low hydrogen values have not been accounted for satisfactorily; they are partly due to the presence of some non-hydrolysable matter, possibly an amorphous form of (C).

When (E) has been prepared from diphenylsilicon dichloride of about 95—97% purity (compare Kipping and Murray, *loc. cit.*),† the product after two precipitations contains about 15·1% of silicon, consists mainly of (E_1), and does not give phenol on hydrolysis; the isolation of (E_1) then presents no very great difficulty. The earlier crude preparations of (E), however, contained only 12·5—14% of silicon, and the isolation of (E_1) required a prolonged series of fractional precipitations whereby a large proportion of rather more soluble glue-like matter was gradually separated; this material gave phenol and ethyl alcohol on hydrolysis.

The Silicohydrocarbon (E_1).—Many preparations of the composition $[SiPh_2]_n$ were fractionally extracted with boiling alcohol or boiling light petroleum, precipitated from hot phenol with alcohol, etc., but their properties underwent but little change, and no crystalline product, except perhaps traces of (B), could be isolated. The fractional diffusion of an acetone solution through unglazed earthenware also failed to afford crystals.

The preparations have no definite melting point but gradually liquefy over a range of 20° or 30° or so, beginning to sinter from about 110° to 130°; they are miscible with cold ether, benzene, chloroform and many other solvents, from all of which they separate as "glues," which very gradually become brittle, but they are only sparingly soluble in boiling light petroleum and very sparingly in boiling alcohol or glacial acetic acid. Preparations kept in the solid state during 4—5 years are still miscible with cold acetone.

(E_1) does not react appreciably with iodine in cold benzene

* The silica is very hygroscopic and may absorb as much as 28·4% of water on exposure to the air.

† It is no easy matter to ascertain whether—or when—the reaction with sodium is at an end. The toluene solutions of the product, which give no sign of a green flame with copper, afford an aqueous extract containing halogen. This seems to be partly present as sodium chloride, which is slightly soluble in toluene solutions of (E). The heating was usually stopped when an aqueous extract gave a neutral reaction to litmus, but even this test seems to be untrustworthy, and (E) may still contain halogen. If the heating with sodium is continued beyond a certain point, the filtered toluene solution gives an alkaline reaction, and the crude (E), obtained by evaporation, effervesces when treated with (undried) acetone; if this occurs, the fractional precipitation of the acetone solution with alcohol (after removing B) yields a large proportion of trianhydrotrisdiphenylsilicanediol, and the isolation of (E_1) is difficult or impossible.

solution; in carbon tetrachloride solution, a little bromine is absorbed, but many hours elapse before the proportion reaches $Br_2 : [SiPh_2]_2$. In some cases traces of a crystalline bromo-compound were obtained, but the principal solid product was a very little rhomboidal oxide, probably formed by the hydrolysis of a dibromide, $SiPh_2Br{\cdot}SiPh_2Br$, and subsequent condensation of the diol; the reaction seemed also to involve the partial separation of phenyl groups as bromobenzene without precipitation of silica.

When (E_1), partly dissolved and partly suspended in glacial acetic acid, is cautiously oxidised with nitric acid, it yields the rhomboidal oxide, but is almost entirely converted into crystalline and oily condensation products of diphenylsilicanediol.

Formation of (B) and (A) from (E).—A solution of (E) (30—35 g.) in undried commercial ether, which had been kept about 3 weeks in a closed vessel and then filtered from the deposit of (B), was evaporated and the residue heated in a very short-necked (2″) flask under 6 mm. pressure. At first a little (0·2 g.) diphenyl came over; the temperature then rose rapidly to about 300° (thermometer in liquid) and a very slow "distillation" commenced, fractions, each of about 1½ c.c., being collected at 300—330°, 330—350° and 350—360°. The temperature then rose slowly to 400° (5 mm.), but no further distillation occurred and crystals which had been splashed on to the sides of the flask had not liquefied when the heating was stopped.

When cold, the glue-like mass was treated with acetone and left over-night; most of it dissolved, leaving some crystalline matter (about 2 g.), which was washed with acetone. This product was almost completely soluble in cold chloroform, and was reprecipitated by acetone in short, rectangular prisms which were identified as those of octaphenyl*cyclo*silicotetrane (B) by a direct comparison. The portion insoluble in cold chloroform (about 0·1 g.) crystallised from benzene in short, flat prisms and was proved to be octaphenylsilicotetrane (A) by its behaviour towards iodine and in other ways.

In order to prove that the cyclic silicohydrocarbon (B) had not been held in solution by the liquid "distillate" of (E), some of it was dissolved in a portion of this distillate; the solution, diluted with ether or with acetone, gave an immediate precipitate and apparently the whole of the dissolved (B) was deposited.

Of the three fractions referred to above, the two more volatile ones fumed very slightly in the air and contained halogen.* All three fractions deposited traces of trianhydrotrisdiphenylsilicanediol, reduced an aqueous solution of silver nitrate in a marked manner, and gave hydrogen very readily with acetone and aqueous

* The heating with sodium had been continued during at least 6 hours.

alkali. The whole of this thick, oily " distillate " was poured into glacial acetic acid (about 4 vols.)—in which it was only very sparingly soluble—and then a few drops of concentrated nitric acid were added; oxidation set in very readily and after the non-homogeneous mixture had been warmed on the water-bath during some 2 hours and then cooled, a considerable quantity of crystalline matter separated very slowly from the oily layer. This crystalline product, purified by recrystallisation from alcoholic chloroform, was conclusively proved to be triphenylsilicol by analysis, mixed melting-point determinations, etc., and by converting it into triphenylsilicyl oxide (m. p. 222—223°).

The fact that this oil gave a large proportion (at least 25%) of triphenylsilicol on oxidation, whereas undistilled (E) gives no such product, seemed to prove that a migration of phenyl groups had occurred without separation of silicon or silica. The acetone solution of the residue from the distillation, fractionally treated with alcohol, gave precipitates of much the same character as (E_1); they were, however, less readily soluble in acetone, and contained 16—17% of silicon ($SiPh_2$ requires 15·4%), the percentage increasing with the duration of the " distillation."

In the hope of confirming these results, another preparation of (E), which had been kept in dry ethereal solution during 19 days, was separated from the usual deposit, and the crude (E) (12 g.) obtained on evaporation of the solvent was heated under 1—1·5 mm. (thermometer in the liquid) in a very short-necked flask. From about 283° to 310°, about 1½ c.c. of a thick oil very slowly collected in the receiver, but there was no separation of crystals from the distillate or from the residue, even when the latter was treated with acetone.

The distillate contained only traces of halogen, reduced an aqueous acetone solution of silver nitrate, and gave triphenylsilicol on oxidation with a glacial acetic acid solution of nitric acid; when treated with alkali in acetone solution, it gave hydrogen readily at the ordinary temperature, and, after some of the solvent had been expelled, crystals of triphenylsilicol were deposited; these, left on porous earthenware, without having been freed from alkali, passed into crystals of the silicyl oxide. The mother-liquor from the silicol, warmed again with alcohol and alkali, gave further deposits of triphenylsilicyl oxide, and finally at least 80% of a portion of the original distillate was transformed into this compound.

All attempts to isolate triphenylsilicol or the oxide from other portions of this distillate without using nitric acid or alkali were unsuccessful; the oil certainly did not contain the oxide, nor did it give any crystals of the latter after it had been heated for a long

time with alcohol and hydrochloric acid. The residue from this "distillation" solidified to a very brittle resin, which behaved on hydrolysis quite differently from ordinary samples of (E), inasmuch as it gave, in addition to diphenylsilicanediol, a considerable proportion of triphenylsilicyl oxide. A direct comparison of two samples of the same preparation of (E), one of which had been heated at about 350° for some time, proved that only the latter gave triphenylsilicyl oxide on hydrolysis; from 3·7 g. of the unheated material, only about 0·25 g. was not ultimately convertible into diphenylsilicanediol or other products soluble in aqueous alkali.

It must be concluded from these results that at high temperatures some of the molecules composed entirely of $SiPh_2$ groups are decomposed, giving triphenylsilicyl, $SiPh_3$·, or some other compound containing a $SiPh_3$-group.

Conversion of Octaphenylcyclosilicotetrane into an Amorphous Form.—When pure (B) is very rapidly heated in a test-tube over a free flame in an inert atmosphere, it can be partly melted, and when the cooled product is treated with cold acetone, the melted portion dissolves, leaving the crystalline matter; by repeating these operations, the whole of any sample of (B) can be obtained in solution in about 1—2% of the volume of solvent which would have been required to dissolve the crystals, but not more than 0·1 g. of (B) should be heated at a time. The acetone solution begins to deposit crystals of pure (B) either within a few minutes or only after some hours, and this deposition may continue during many days: the filtered solution gives with alcohol an apparently amorphous, flocculent precipitate, which, when separated and freed from solvent, melts very indefinitely from 110° to 150° and contains 15·4% of silicon ($SiPh_2$ requires Si, 15·5%); the molecular weight in camphor was found to be 1500, whereas under the same conditions crystalline (B) gives the normal results for $[SiPh_2]_4$ (J., 1924, **125**, 2291). The alcoholic acetone filtrate from the amorphous precipitate gives on evaporation a little more of an apparently identical product.

As there is no charring, or evolution of vapour, or separation of insoluble matter when (B) is thus heated, and as the whole of the product seems to be silicohydrocarbon $[SiPh_2]_n$, it is concluded that the soluble amorphous product is merely a form of octaphenyl-*cyclo*silicotetrane in which the molecules have become entangled with one another. It is not suggested that this form, produced by melting (B), is identical with (E_1); it seems to differ from (E_1) in being more readily and more completely transformed into the crystalline variety, and may be regarded rather as a mixture of (B) molecules analogous to that which is contained in the original

toluene solution of (E) and from which a considerable proportion of (B) is rapidly precipitated on the addition of acetone.

The author has been assisted in this investigation by J. E. Sands and R. Vyle, M.Sc., and has also received financial help for the purchase of diphenylsilicon dichloride (kindly supplied by Boots' Pure Drug Company) from the Government Grant Committee of the Royal Society: for all such assistance he wishes to record his indebtedness.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 9th*, 1927.]

CCCLXIII.—*Organic Derivatives of Silicon. Part XXXIV. The Action of Sodium on Phenoxydiphenylsilicyl Chloride.*

By FREDERIC STANLEY KIPPING.

SINCE the product (E) of the action of sodium on diphenylsilicon dichloride may give on hydrolysis appreciable quantities of phenol (this vol., p. 2724), it was inferred that the dichloride, in spite of its constant boiling point, might be contaminated with phenoxyphenylsilicon dichloride, phenoxydiphenylsilicyl chloride, or diphenoxydiphenylsilicane. It is known that atmospheric oxidation may occur during the preparation of magnesium phenyl bromide (Porter and Steel, *J. Amer. Chem. Soc.*, 1920, **42**, 2650) and the resulting Grignard reagent, containing magnesium phenoxy-bromide, might give rise to phenoxy-derivatives if used for the preparation of diphenylsilicon dichloride from silicon tetrachloride.

The action of phenol on diphenylsilicon dichloride was therefore studied, partly in order to observe the boiling points of two of the phenoxy-derivatives just mentioned, but mainly in the hope that by the fractional distillation of the product some other unknown impurity in the dichloride might be isolated and identified.

The results gave no support to the inference that the dichloride formed a constant-boiling mixture with either of these phenoxy-derivatives, and the product—consisting of phenoxydiphenylsilicyl chloride, diphenoxydiphenylsilicane, and unchanged diphenylsilicon dichloride—could be separated into its components by fractional distillation; no fraction representing the long sought-for impurity in the dichloride (compare Kipping and Murray, this vol., p. 2734) was obtained.

The action of sodium on phenoxydiphenylsilicyl chloride was then examined in the hope that symmetrical diphenoxytetraphenyl-

silicoethane would be produced, just as hexaphenylsilicoethane is formed from triphenylsilicyl chloride (Kipping, P., 1911, **27**, 144); the results were quite unforeseen. The products, isolated with the aid of anhydrous solvents, were octaphenylsilicotetrane,

$$-SiPh_2\cdot SiPh_2\cdot SiPh_2\cdot SiPh_2-$$

(Kipping and Sands, J., 1921, **119**, 830; Kipping, J., 1923, **123**, 2590), diphenoxyoctaphenylsilicotetrane, $PhO\cdot[SiPh_2]_4\cdot OPh$, and diphenoxydiphenylsilicane; from the remaining material, with the use of other solvents not free from water, phenol, diphenylsilicanediol, a considerable proportion of an apparently amorphous solid, which is possibly $PhO\cdot[SiPh_2]_4\cdot OH$, and a very viscous oil, possibly $PhO\cdot SiPh_2\cdot SiPh_2\cdot OPh$, were obtained.

The formation of octaphenylsilicotetrane suggested that the phenoxy-chloride was contaminated with diphenylsilicon dichloride; but in subsequent preparations, using only material which, from its boiling point and from analyses, was the pure phenoxy-derivative, the three products named above were again obtained, apparently in the same yields as before; moreover, that of the silicohydrocarbon seemed to be about as large as if diphenylsilicon dichloride had been used instead of the phenoxy-chloride.

Now the supposed phenoxy-chloride cannot be a mixture of equal quantities of diphenylsilicon dichloride and diphenoxydiphenylsilicane. The product of the action of phenol (1 mol.) on the dichloride is not a liquid of constant boiling point, but distils over a range of about 100°. Further, the phenoxy-chloride is immediately and completely soluble in a cold 5% solution of potassium hydroxide, whereas the diphenoxy-derivative is practically insoluble in, and is only slowly hydrolysed by, such a solution; a prepared solution of the diphenoxy-compound in the dichloride gives crystals of the former when it is added to cold aqueous alkali. Another important fact, which seems to show that the phenoxy-chloride is not converted into a mixture of the dichloride and the diphenoxy-derivative at any stage of the reaction, is that, so far as can be ascertained, the other products of the action of sodium on diphenylsilicon dichloride, namely, octaphenyl*cyclo*silicotetrane (B) and the complex silicohydrocarbons (C) and (D) (Kipping, J., 1924, **125**, 2291), are not formed from the phenoxy-chloride. Finally, the production of diphenoxyoctaphenylsilicotetrane proves that a phenoxy-derivative takes part in the reaction, but apparently diphenoxydiphenylsilicane is not attacked by sodium even at temperatures above 110°.

Although, therefore, it must be concluded that octaphenylsilicotetrane and its diphenoxy-derivative are obtained from the phenoxy-chloride, the mechanism of their formation is obscure. The pro-

duction of diphenoxydiphenylsilicane seems to prove that at one stage sodium phenoxide is formed, and reacts with unchanged phenoxy-chloride to give the diphenoxy-derivative; this view is confirmed by the fact that sodium phenoxide is present in the blue insoluble residue (p. 2731). It does not seem likely, however, that symmetrical diphenoxytetraphenylsilicoethane is produced and then reacts with sodium to give sodium phenoxide, because, although some ethers are attacked by the metal (Schorigin, *Ber.*, 1926, **59**, 2510), diphenoxydiphenylsilicane and diethoxydiphenylsilicane (Kipping and Murray, this vol., p. 2736) appear to be unacted on. It may be suggested, therefore, that the phenoxy-chloride is decomposed by sodium, giving first $SiPh_2Cl{\cdot}SiPh_2Cl$ and then

$$SiPh_2Cl{\cdot}[SiPh_2]_2{\cdot}SiPh_2Cl,$$

and that a part of the latter is transformed into octaphenylsilicotetrane, whilst some of it reacts with sodium phenoxide to form diphenoxyoctaphenylsilicotetrane. The absence from the reaction product of (B), (C), and (D), however, does not accord with these assumptions, since it would seem to be highly probable that (B) at any rate would also be formed from such dichlorides.

Experimental.

Interaction of Phenol and Diphenylsilicon Dichloride.—Phenol (1 mol.), dissolved in a little benzene, is dropped slowly into diphenylsilicon dichloride * at about 150°, hydrogen chloride being immediately evolved; the liquid is then heated at about 200° until the evolution ceases (about 3 hours). The product deposits crystals of diphenoxydiphenylsilicon when it is kept at 0°, but it is more convenient to separate the latter by distillation (40 mm.). The first fraction (15—20%) is collected at about 200—240°, a large fraction (about 45%) at 250—260°, and a second large fraction at 280—310°, leaving a small residue. The liquid collected from 200—240°, when again treated with about one-half of its weight of phenol, gave further quantities of the two phenoxy-derivatives, but no fraction having the boiling point of diethoxydiphenylsilicane, a possible impurity in the diphenylsilicon dichloride, could be isolated.

Phenoxydiphenylsilicyl chloride, $SiPh_2Cl{\cdot}OPh$, obtained by the further fractionation of the liquid, b. p. about 250—260°, is a thick oil which barely fumes in the air and is miscible with light petroleum and other anhydrous solvents; it boils at 252—254°/40 mm. [Found: Cl, 11·0, 10·9, 11·2, 11·1 (four different preparations);

* Three samples of the dichloride (b. p. 224—226°/100 mm.) were used, containing 25·2, 24·8, and 25·7% of chlorine, respectively. (Calc. for $SiPh_2Cl_2$: Cl, 27·9%.) Compare Kipping and Murray, *loc. cit.*

Si, 9·0. $C_{18}H_{15}OClSi$ requires Cl, 11·4; Si, 9·1%]. It is immediately and completely soluble in a 5% solution of potassium hydroxide, giving the potassium derivatives of phenol and of diphenylsilicanediol. When left exposed to moist air, it is gradually converted into a solid, smelling strongly of phenol, which after recrystallisation from benzene consists of trianhydrotrisdiphenylsilicanediol.

Diphenoxydiphenylsilicane, $SiPh_2(OPh)_2$, separates in crystals from the fraction collected above 280°, but as it is always mixed with a considerable proportion of the oily phenoxy-chloride the crude product is fractionated again; it then crystallises from light petroleum in massive, colourless prisms and octahedra, m. p. 70—71° (Found: Si, 7·7, 7·8. $C_{24}H_{20}O_2Si$ requires Si, 7·7%). It is very readily soluble in ether, chloroform, benzene, or acetone, but only moderately soluble in cold alcohol. It can be recrystallised from the last-named solvent, but the crystals seem rather sticky and melt at 65—69°, doubtless owing to some very slight hydrolysis having occurred; if attempts are made to recrystallise the impure substance, containing phenoxy-chloride, from alcohol, complete decomposition results, and trianhydrotrisdiphenylsilicanediol may separate. When boiled with water for a short time, the diphenoxy-derivative is not appreciably hydrolysed, owing to its insolubility; it is also relatively stable towards a 5% solution of sodium hydroxide, but it is very readily hydrolysed in presence of acetone or alcohol with separation of trianhydrotrisdiphenylsilicanediol, whilst sodium phenoxide remains in solution. The fact that diphenoxydiphenylsilicane is present in a toluene solution which has been boiled during several hours with excess of sodium, is conclusive evidence of its stability under such conditions, and yet when an apparently pure specimen, recrystallised from light petroleum and melting sharply at 70—71°, is heated with sodium and a little toluene a distinct effervescence occurs and the metal is coated with a white powder. The reaction, however, soon ceases and the rest of the phenoxy-compound is unaltered. It would seem from these observations, repeated several times, that the recrystallised substance contains a small proportion of diphenylsilicanediol or phenoxyhydroxydiphenylsilicane.

Action of Sodium on Phenoxydiphenylsilicyl Chloride.—Freshly distilled phenoxy-chloride is dissolved in dry toluene (about 4 vols.), excess of sodium added, and the whole heated; an exothermic reaction soon sets in and the metal becomes coated with a blue crust similar to that obtained with diphenylsilicon dichloride under the same conditions. After the solution has boiled during 2—3 hours it contains some colourless crystals and seems to be free from phenoxy-chloride when tested with a copper wire. The hot solution

is filtered, the blue residue (I) washed with toluene, and the combined filtrate and washings are evaporated under reduced pressure. The almost colourless, oily product, when mixed with a little light petroleum (b. p. 50—60°), gives a crystalline precipitate (II), and the filtered solution, diluted with more petroleum, gives an oily separation (III); the clear petroleum solution, decanted from the oil, gives a further oily deposit (IV) when it is kept at 0°, but even then it contains a considerable quantity of product (V).

Isolation of octaphenylsilicotetrane. The blue residue (I) of sodium, sodium chloride, and sodium phenoxide is added in small portions to alcohol–acetic acid, the solution being kept acid; the insoluble matter, after being well washed with water, consists of almost pure octaphenylsilicotetrane, which was fully identified by a mixed melting-point determination, by its characteristic action with nitrobenzene and with iodine (compare Kipping and Sands, *loc. cit.*), and in other ways. So far as could be ascertained, the silicohydrocarbons (C) and (D) which are formed together with octaphenylsilicotetrane by the action of sodium on diphenylsilicon dichloride are not produced from the phenoxy-chloride; all the organic matter from the blue residue is soluble in boiling benzene, and although the final mother-liquors and the deposits were carefully examined, not a single crystal of (C) could be detected (compare Kipping, J., 1924, **125**, 2294).

Diphenoxyoctaphenylsilicotetrane, $PhO\cdot[SiPh_2]_4\cdot OPh$. The precipitate (II) consists of diphenoxyoctaphenylsilicotetrane and octaphenylsilicotetrane. The former is extracted with boiling benzene, in which it is much the more soluble, and is then recrystallised from boiling chloroform and again from benzene, from which it separates in well-defined, rhomboidal pyramids and in prisms, m. p. 215—216° (Found: Si, 12·3; C, 78·1; H, 5·2; *M*, in camphor, 1083, 1040. $C_{60}H_{50}O_2Si_4$ requires Si, 12·3; C, 78·7; H, 5·5%; *M*, 915). The diphenoxy-compound is decomposed when it is heated with piperidine and a concentrated solution of sodium hydroxide, giving the sodium derivatives of phenol and diphenylsilicanediol, with evolution of hydrogen. [Hydrogen value (compare Kipping and Sands, J., 1921, **119**, 848) found, 69·0, 67·4, 70·5; calc. for $PhO\cdot[SiPh_2]_4\cdot OPh + 10NaOH = 2PhONa + 4SiPh_2(ONa)_2 + 2H_2O + 3H_2$, 73·1].

Diphenoxyoctaphenylsilicotetrane is practically insoluble in ether, acetone, alcohol, and glacial acetic acid, and is far less soluble in cold benzene and chloroform than octaphenyl*cyclo*silicotetrane (B): it is so like the rhomboidal oxide (Kipping and Sands, J., 1921, **119**, 844) in crystalline form, solubilities, and melting point that it might well be mistaken for the latter, but its mixture with the rhomboidal

oxide melts at 208—211°. It is very readily soluble in boiling aniline, from which it separates on cooling in small prisms. It seems to be unchanged when it is heated during 1—2 hours with a glacial acetic acid solution of nitric acid, and it is so slowly hydrolysed when it is boiled with an alcoholic solution of hydrochloric acid that after about 20 hours' heating most of the substance remains undissolved and unchanged; the presence of phenol in the resulting pink solution can, however, be proved. The stability of the compound may be attributed to steric hindrance; its formation from the phenoxy-chloride under the above-described conditions is all the more noteworthy in view of the non-production of decaphenylsilicotetrane by the action of magnesium phenyl bromide on octaphenylsilicotetrane di-iodide (Kipping, J., 1923, **123**, 2602).

Other products from the phenoxy-chloride. From the combined oily separations (III) and (IV), by fractional extraction with light petroleum, diphenoxydiphenylsilicane was isolated and then, with the aid of a mixture of acetone and light petroleum, some diphenylsilicanediol, which had no doubt been formed by the hydrolysis of the diphenoxy-derivative during the prolonged fractionation with undried solvents. The mother-liquors from the diol gave on evaporation a glue-like mass, smelling strongly of phenol, which did not crystallise in the course of some weeks; after being washed with water and dissolved in acetone, this glue was precipitated by alcohol as a white curd, very similar in properties to the precipitates of (E_1) obtained in like manner (this vol., p. 2723). This product was redissolved and reprecipitated many times and then repeatedly extracted with warm alcohol, in which it was only very sparingly soluble; the warm glue was then drawn into threads and when cold the brittle mass was powdered and freed from solvent. Two different preparations gave Si, 13·3 and 13·6%, respectively; when hydrolysed with piperidine and sodium hydroxide, they gave hydrogen, sodium phenoxide, and the sodium derivative of diphenylsilicanediol, and the following hydrogen values: 82·7, 80·3, 81·1. These results agree with those required for

$$HO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OPh,$$

but the physical properties of the material do not seem to correspond with such a formula; possibly the substance is an oxide, $(PhO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot})_2O$.

The light petroleum solution of the product (V) gave on evaporation a very thick, colourless oil, which in the course of some months deposited a considerable proportion of diphenoxydiphenylsilicane; this was removed by repeated extraction with warm alcohol. The residue was then completely and readily soluble in cold light petroleum (b. p. 40—50°), from which it separated as an oil. This product

contained 10·9% of silicon and is possibly impure symmetrical diphenoxytetraphenylsilicoethane, $PhO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OPh$, which requires Si, 10·3%; it gave hydrogen with acetone and sodium hydroxide, and the alkaline solution then contained sodium phenoxide and the sodium derivative of diphenylsilicanediol.

The author wishes to express his indebtedness to Mr. R. Vyle, M.Sc., who rendered very efficient assistance during this work, and to the Government Grant Committee of The Royal Society for funds from which to buy diphenylsilicon dichloride from Boots' Pure Drug Co.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 9th,* 1927.]

CCCLXIV.—*Organic Derivatives of Silicon. Part XXXV. The Preparation of Diphenylsilicon Dichloride: "Grignard" Ether and its Action on Silicon Tetrachloride.*

By FREDERIC STANLEY KIPPING and ARTHUR GEORGE MURRAY.

THE analysis of the first sample of diphenylsilicon dichloride gave 28·0% of chlorine (Calc. for $SiPh_2Cl_2$: Cl, 27·9%).* Large quantities of this compound were used later for the preparation of diphenylsilicanediol, and during a very careful examination of the latter and of its condensation products (J., 1912, **101**, 2108, 2125) there was no indication of unknown impurity in the dichloride. When, however, it was discovered that the product (E) contained phenoxy-compounds (this vol., p. 2720), several samples of the dichloride were examined and found to contain only 23—24% of chlorine; † they also gave 3—4% of phenol on hydrolysis.

The preparation of the magnesium phenyl bromide used in making the silicon compound was then carried out in an atmosphere of nitrogen (compare this vol., p. 2728), as was also, later on, the actual preparation of the dichloride; the samples thus obtained (b. p. 223—224° or 224—225°/100 mm.) gave inappreciable quantities of phenol, but still contained only 25·5—26% of chlorine, a proportion which could not be altered by further fractionation under various pressures. The silicon percentages in such samples agreed very closely with that required for $SiPh_2Cl_2$, an indication that the

* J., 1912, **101**, 2114. The sample was prepared and purified by one of us (F. S. K.), but was analysed under direction by a senior student, ignorant of the nature of the substance.

† The purchased samples were invoiced as having a purity of 80–90%.

impurity might be $SiPh_2(OEt)_2$ or $SiPh_2(OEt)Cl$, formed from traces of alcohol in the large volume of ether used in their preparation; but no matter how thoroughly the Grignard ether was freed from alcohol, the purity of the dichloride could not be increased and all samples gave alcohol on hydrolysis.

The behaviour of silicon tetrachloride towards ether was then studied (the tetraiodide is known to react; Friedel, *Ber.*, 1872, **5**, 27) and it was found that even at the ordinary temperature a slight action occurs, probably as follows: $SiCl_4 + Et_2O = SiCl_3 \cdot OEt + EtCl$. The difficulty of preparing pure diphenylsilicon dichloride is therefore almost certainly due to the formation of ethoxydiphenylsilicyl chloride, which cannot be separated by distillation (p. 2736).

As a solution of magnesium phenyl bromide could not be obtained without the use of ether, the method of preparation of the dichloride was modified so as to limit the interaction of the ether and the tetrachloride. The results were fairly satisfactory, but the product still contained a small proportion of some ethoxy-compound.

The fact that ether reacts with silicon tetrachloride probably accounts for previous difficulties in preparing various organic derivatives of silicon. Thus from the product of the interaction of magnesium ethyl bromide and the tetrachloride, it may not be hard to obtain ethylsilicon trichloride, but the isolation of the di- and the tri-ethyl derivatives by fractional distillation is a very troublesome task (J., 1909, **95**, 311); the difficulty of preparing a pure sample of phenylethylsilicon dichloride (J., 1907, **91**, 217) is also possibly due to the contamination of the product with ethoxyphenylethylsilicyl chloride. In the case of a crystalline product, the formation of some ethoxy-compound would not matter so much, as the impurity would doubtless remain in the mother-liquor; this has been proved to be so in the case of dibenzylsilicon dichloride, since the liquid fractions from the crude preparation give ethyl alcohol on hydrolysis.

EXPERIMENTAL.

For the detection of phenoxy- and ethoxy-groups in an ordinary sample of diphenylsilicon dichloride, the latter is dropped into excess of a 5% solution of sodium hydroxide, and a small proportion of the liquid is then distilled and tested for alcohol; the residue is acidified and again distilled and the distillate is treated with bromine water. Samples of the dichloride prepared by the method described later do not give a recognisable quantity of tribromophenol.

Interaction of Ether and Silicon Tetrachloride.—Very carefully

purified ether was heated under reflux during about 4 hours with an equal volume of silicon tetrachloride; about one-half of the liquid was then distilled and the residue was treated with an excess of sodium hydroxide solution and again distilled; the first small portion of the aqueous distillate gave a distinct but very slight iodoform reaction. By heating the recovered ether (20 c.c.) with about 5% of silicon tetrachloride in a sealed tube during about 8 hours at 100° and then proceeding as before, about four times as much iodoform was obtained, but even under these conditions the quantity was only about 5 mg. The interaction also occurs at the ordinary temperature; after 30 c.c. of ether had been left with about 5 c.c. of silicon tetrachloride during 3 days and most of the ether then distilled off, the residue, on hydrolysis, gave enough alcohol to afford a very slight precipitate of iodoform, and the ether which had been distilled from the mixture, treated again with the tetrachloride, gave a further quantity of the product which yielded alcohol; these processes were repeated four times, with the ether recovered from each previous treatment, and iodoform was obtained, apparently in much the same quantity, after each set of operations.* As the precipitate of iodoform was not appreciably larger than usual when the mixture had been kept during several weeks, it would seem that the reaction is reversible.

Diethoxydiphenylsilicane, $SiPh_2(OEt)_2$, was prepared in order to compare its boiling point with that of diphenylsilicon dichloride. Carefully dehydrated alcohol, in slight excess, was added to the dichloride; only a feeble evolution of hydrogen chloride occurred and two layers were formed, but after having been heated under reflux during 6—8 hours the liquid became homogeneous and was then distilled (100 mm.). The product still contained a little chlorine, and was therefore heated again with a small proportion of alcohol and then fractionated; practically the whole passed over at 217—218°, and a considerable quantity of the preparation gave only an insignificant reaction with an aqueous solution of silver nitrate [Found: Si, 10·4. $SiPh_2(OEt)_2$ requires Si, 10·4%]. The b. p. of the diethoxy-compound differs only very little from that of the dichloride,

$SiPh_2(OEt)_2$	197—198°/50 mm.	217—218°/100 mm.	302—304°/767 mm.
$SiPh_2Cl_2$	199—202°/50 mm.	222—224°/100 mm.	302—305°/757 mm.

* A blank experiment in which ether alone was heated under reflux with a solution of sodium hydroxide during 4 hours, and the alkaline solution was then tested for alcohol, gave a negative result and did not confirm the statement in Allen's "Commercial Organic Analysis" (vol. I, p. 179) that ether kept in presence of moisture generates traces of alcohol.

and it may therefore be deduced that that of the ethoxy-chloride, $SiPh_2Cl{\cdot}OEt$, would differ even less, so that its separation from the dichloride by distillation would be impossible.

Diethoxydiphenylsilicane is specifically heavier than water and is miscible with the common solvents; it seems to be unchanged when it is left during some hours with a 5% solution of potassium hydroxide, but it is quickly hydrolysed by an alcoholic solution and when only a little alkali is present trianhydrotrisdiphenylsilicanediol may separate in crystals; it is also slowly hydrolysed by dilute sulphuric acid. It appears to be unchanged by sodium at 100°.

Preparation of Diphenylsilicon Dichloride.—Silicon tetrachloride (170 g.), diluted with benzene (3 vols.), is placed in a bulb provided with three tubulures, which is fitted with a stirrer and a reflux condenser and is connected through a dropping-funnel with the apparatus for the preparation of magnesium phenyl bromide ($2\frac{1}{4}$ mols.). The air in the whole apparatus is displaced with dry nitrogen and the Grignard reagent is then prepared at 0°, the minimum quantity of ether being used. When about one-half of the magnesium has been dissolved, the ethereal solution is drawn into the exhausted dropping-funnel and is then slowly added to the well-cooled and stirred tetrachloride while the remainder of the Grignard reagent is being made. This portion is then drawn into the funnel as before and added to the tetrachloride, so that at no stage is there any possibility of oxidation. After the product has been stirred during a further period of about 30 minutes, as much ether as possible is distilled off on a water-bath, the operation lasting about 3 hours. More benzene (2 vols.) is then added and the magnesium salts are separated in the usual apparatus (J., 1907, **91**, 216) and well washed with benzene. The combined filtrate and washings give on evaporation such a small deposit of magnesium salt that a second filtration is unnecessary (J., 1912, **101**, 2114) and the product can be directly fractionated. Samples thus obtained contain 27·2—27·3% of chlorine.

The authors wish to express their thanks to the Government Grant Committee of the Royal Society for funds which enabled them to purchase supplies of diphenylsilicon dichloride from Boots' Pure Drug Co., Ltd.

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CCCLXV.—*The Condensation of* o-*Aminothiophenol with* αβ-*Unsaturated Acids.*

By WILLIAM HOBSON MILLS and JAMES BELL WHITWORTH.

IN the course of some experiments carried out with *o*-aminothiophenol with the view of synthesising a carbothiocyanine dye (J., 1922, **121**, 455), we found that this base reacted in an unexpected manner with glutaconic acid. The two substances interacted very readily when heated together, but the product of the reaction was not the anticipated benzthiazole derivative; it was a new compound formed by the condensation of one molecule of glutaconic acid and one molecule of aminothiophenol, with the elimination of one molecule of water, as shown in the equation

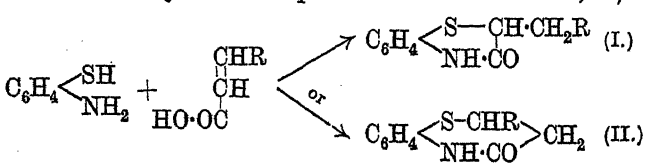
$$C_6H_7NS + C_5H_6O_4 = C_{11}H_{11}O_3NS + H_2O.$$

It was a monobasic acid and it showed none of the reactions characteristic either of the ethylenic linking, the thiol group, or the amino-group. In the interaction, therefore, both the thiol group and the amino-group of the aminothiophenol and the ethylenic linking and one of the carboxyl groups of the glutaconic acid are concerned. That addition of some group to the ethylenic linking had occurred was further indicated by the fact that the new compound was resolvable into antimeric optically active forms, for it would seem that the only way in which an asymmetric carbon atom could be produced in its molecule would be through addition to this linking.

The behaviour of the following αβ-unsaturated acids towards *o*-aminothiophenol was then examined: acrylic, crotonic, and cinnamic acids, and they were all found to react with it similarly to glutaconic acid.

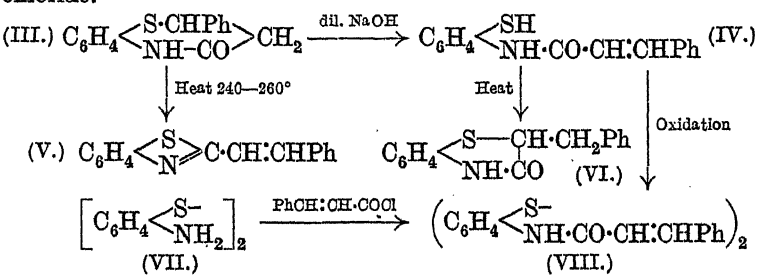
There are four ways in which the observed condensations might occur:

In the first place, *addition of the thiol group* of the aminothiophenol to the ethylenic linking of the acid might take place, accompanied by condensation between the amino- and carboxyl groups. This would give two possible formulæ, according as the sulphur was attached (1) to the α-carbon atom (formation of a ketodihydro-1 : 4-benzthiazine derivative, I), or (2) to the β-carbon atom (formation of a ketotetrahydro-1 : 5-heptabenzthiazine derivative, II).



Alternatively, *addition of the amino-group* of the aminothiophenol to the ethylenic linking of the acid might occur, with condensation between the carboxyl and thiol groups. This would give two further possible constitutions—(3) and (4)—according to whether the nitrogen was attached to the α- or the β-carbon atom.

We found that actually condensation of the amino-group of the aminothiophenol with the carboxyl group of the acid had occurred and that therefore addition of the thiol group to the ethylenic linking had taken place. This was established by examining the compound obtained from cinnamic acid and aminothiophenol. The resulting compound was an indifferent substance, but on being heated with dilute alkalis it dissolved gradually, forming a yellow solution from which carbon dioxide precipitated an isomeric compound, which could be proved to have the constitution (IV); for it had all the properties of a thiophenol, being soluble in alkalis, giving a mercuric derivative with mercuric chloride, and being converted by atmospheric oxygen and various other oxidising agents—iodine, ferric chloride, or hydrogen peroxide—with loss of one atom of hydrogen into a compound insoluble in alkalis, which was shown to be the disulphide (VIII), since it could be synthesised by introducing a cinnamoyl group into each of the two amino-groups of *oo'*-diaminodiphenyl disulphide (VII), by treatment with cinnamoyl chloride.

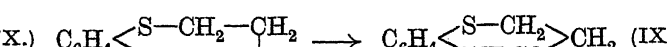


These observations limit the possible formulæ for the compound to (I), the ketodihydrobenzthiazine, or (II), the ketotetrahydroheptabenzthiazine (R = Ph). The behaviour towards alkalis, however, is different from that recorded for the ketodihydrobenzthiazines, which, according to Unger and Graff (*Ber.*, 1897, **30**, 2387), undergo, on boiling with potash, fission of the heterocyclic ring between the -NH- and -CO- groups. Further, the compound could be shown definitely not to be a ketodihydrobenzthiazine, since it was different from the *keto-2-benzyldihydrobenzthiazine* (VI) we obtained, according to the general method described by Unger and Graff (*loc. cit.*) for preparing these compounds, by heating *o*-aminothiophenol with α-bromo-β-phenylpropionic acid.

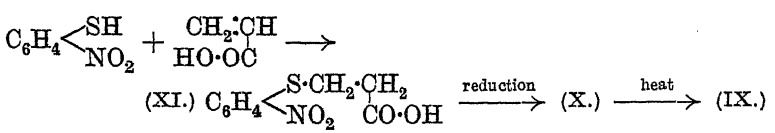
Similarly, our products from acrylic acid and crotonic acid and aminothiophenol are different from the keto-2-methyldihydrobenzthiazine and the keto-2-ethyldihydrobenzthiazine obtained by Unger and Graff from α-bromopropionic acid and α-bromobutyric acid and aminothiophenol; also we found that α-bromoglutaric acid (employed in the form of its ester) gave a different product from that obtained with glutaconic acid.

The compounds in question are therefore ketotetrahydroheptabenzthiazines of the general formula (II).

A final confirmation of the correctness of this conclusion was secured by showing that the compound got by heating aminothiophenol with acrylic acid is identical with the ε-lactam (IX) obtained by Mayer and Horst (*Ber.*, 1923, **56**, 1415) by heating β-2-aminophenylthiolpropionic acid (X), and further by the synthesis of this

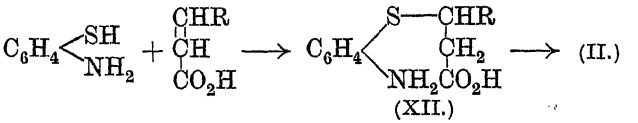


compound from *o*-nitrothiophenol and acrylic acid, as follows, the initial condensation evidently consisting in β-addition of the thiol group of the nitrothiophenol to the ethylenic linkage of the acrylic acid:



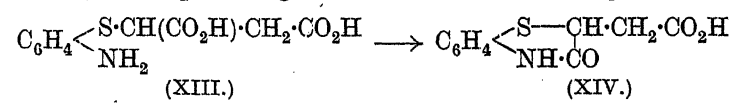
When *cinnamamidothiophenol* (IV) (see scheme on p. 2739) is heated, it is not converted into 1-styrylbenzthiazole (V) as perhaps might have been expected, but ring closure takes place through addition of the thiol group to the ethylenic linkage. The product is, however, not the original ε-lactam (III) (*keto-2-phenyltetrahydroheptabenzthiazine*), but the isomeric δ-lactam (VI) (keto-2-benzyldihydrobenzthiazine), the sulphur becoming attached to the α-carbon atom of the ethylenic linking. The tendency to the formation of a six- rather than of a seven-membered ring thus over-rides the natural tendency of the sulphur atom of the thiol group to attach itself to the β-carbon atom of the ethylenic linking (Posner, *Ber.*, 1907, **40**, 4788). It follows from this fact that, in the interaction of the αβ-unsaturated acids with *o*-aminothiophenol, of the various reactions possible that which takes place with the greatest velocity (excluding of course salt formation between the acid and base) is the addition of the thiol group to the ethylenic linking, the sulphur becoming attached to the β-carbon atom, the resulting aminophenyl-

thiolpropionic acid (XII) passing, at the temperature employed, with loss of water into its ε-lactam :



(XII.)

To test this conclusion, the interactions of *o*-aminothiophenol with maleic acid and with monobromosuccinic acid were studied. In all the other cases investigated, we have seen that a different product was obtained according as *o*-aminothiophenol was heated with a given αβ-unsaturated acid or with the corresponding α-bromo-saturated acid. In this one case, however, identical products should be formed, since in the intermediate product (XIII) arising from maleic acid there is, besides the carboxyl group to which, as in the other cases, the amino-group is in the ε-position, a second carboxyl group to which it is in the δ-position and with which it can consequently react, producing a normal six-membered ring :



(XIII.) (XIV.)

The result was as expected, the same product (3-*ketodihydrobenzthiazine*-2-*acetic acid*, XIV) being obtained by heating either maleic acid or monobromosuccinic acid with *o*-aminothiophenol.

If the ε-lactam (keto-2-phenyltetrahydroheptabenzthiazine, III obtained by heating *o*-aminothiophenol with cinnamic acid is heated to 240—260°, water is eliminated and there is formed, although not very smoothly, 1-styrylbenzthiazole (V). This explains why Hofmann (*Ber.*, 1880, **13**, 1235) had obtained from *o*-aminothiophenol and cinnamic acid this benzthiazole derivative, whilst we had found the product of the reaction to be the ε-lactam; we had worked at 160—170°, whereas Hofmann had heated the mixture on a sand-bath. Hofmann's procedure does not, however, provide an advantageous method for preparing the benzthiazole base : it can be much more readily prepared by treating *o*-aminothiophenol (or, better, its sodium salt) with cinnamoyl chloride in the cold. On the other hand, we found that the corresponding saturated acid, β-phenylpropionic acid, reacted readily with *o*-aminothiophenol to give phenylethylbenzthiazole.

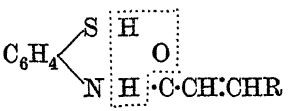
If *o*-aminothiophenol is heated with ethyl cinnamate instead of with cinnamic acid, a higher temperature has to be employed to bring about reaction, and the product is then the δ-lactam (keto-2-benzyldihydrobenzthiazine, VI).

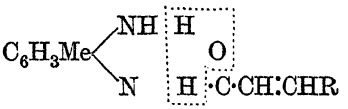
Thus, according as *o*-aminothiophenol is heated with cinnamic

acid, its ester, or its chloride, three different heterocyclic compounds are obtained.

o-Aminothiophenol —(cinnamic acid)→ Ketophenyltetrahydroheptabenzthiazine (III).
o-Aminothiophenol —(ethyl cinnamate)→ Ketobenzyldihydrobenzthiazine (VI).
o-Aminothiophenol —(cinnamoyl chloride)→ Styrylbenzthiazole (V).

The non-formation of a benzthiazole base when *o*-cinnamamidothiophenol (IV) is heated, or when ethyl cinnamate is heated with *o*-aminothiophenol, shows that the attachment of a $-CH{:}CHR$ group, instead of a saturated system, to the carbon of the $-CO{\cdot}NH-$ group in *N*-acyl derivatives of *o*-aminothiophenol makes the elimination of water in the manner shown more difficult.





The corresponding phenomenon was observed by Fichter (*J. pr. Chem.*, 1906, **74**, 316) with the crotonyl and dimethylacrylyl derivatives of 1 : 3 : 4-tolylenediamine.

The ketotetrahydroheptabenzthiazines are readily acetylated when boiled with acetic anhydride. This was also observed by Mayer and Horst, who found (*loc. cit.*) that their ε-lactam reacted easily with acetic anhydride. However, they assigned to the product the formula (XV), which is at variance with the composition we find for it and for the two corresponding derivatives which we have obtained from our analogous ε-lactams; the molecule is actually less by the elements of a molecule of water than this formula indicates. It is also at variance with the chemical character of the compounds: they are neutral and unaffected by cold

(XV.) $C_6H_4\langle^{S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}_{NHAc}$ $\quad$ $C_6H_4\langle^{S-\!-CHR}_{NAc{\cdot}CO}\rangle CH_2$ (XVI.)

$C_6H_4\langle^{S{\cdot}CH_3}_{NH{\cdot}CO}\rangle CH_3$ (XVII.)

sodium carbonate solution. Since, moreover, the acetyl group is readily eliminated on warming with dilute hydrochloric acid or sodium carbonate with regeneration of the original lactam, the constitution of these acetyl derivatives is clearly that represented by (XVI). Their ready formation is in accordance with the fact observed by Ulffers and von Janson (*Ber.*, 1894, **27**, 93) and by Sudborough (J., 1901, **79**, 533) that diacetylation of a primary aromatic amine is particularly easy when there is another substituent group in the ortho-position to the amino-group. These ε-lactams are closely related in constitution to *o*-acetamidothio-

anisole (XVII) (linking of the two methyl groups in which, with removal of two atoms of hydrogen, would yield the ε-lactam of Mayer and Horst), and Mr. G. E. Watts, working in this laboratory, found that *o*-aminothioanisole is readily converted into a diacetyl derivative when heated with acetic anhydride.

An interesting alternation in properties exists between the γ-, δ-, and ε-lactams, benzthiazolone (XVIII), ketodihydrobenzthiazine (XIX), and ketotetrahydroheptabenzthiazine (IX), with respect to

(XVIII.) $C_6H_4\langle^{S-}_{NH}\rangle CO$ $\qquad\qquad$ $C_6H_4\langle^{S—CH_2}_{NH\cdot CO}$ (XIX.)

acetylation. Benzthiazolone (for which a new method of preparation is described in the experimental part) and, as has been stated, the ε-lactam (IX) are readily acetylated when boiled with acetic anhydride, whilst ketodihydrobenzthiazine is not (Unger and Graff, *loc. cit.*).

EXPERIMENTAL.

I. *Glutaconic Acid and* o-*Aminothiophenol.*

4-Ketotetrahydro-1 : 5-heptabenzthiazine-2-acetic Acid (II; R = $CH_2\cdot CO_2H$).—A mixture of glutaconic acid (2·5 g.) and *o*-aminothiophenol (2·5 g.; 1 mol.) was heated in an atmosphere of carbon dioxide at 120—130° for 20 minutes. A vigorous reaction occurred and after a few minutes the whole had set to a crystalline mass, which, recrystallised from dilute alcohol or water, yielded the pure product as thin, colourless, silky needles, m. p. 235—236° (decomp.). Yield, 4 g. (84·4%) (Found : C, 55·5; H, 4·6. $C_{11}H_{11}O_3NS$ requires C, 55·7; H, 4·6%).

The compound dissolves readily in dilute aqueous sodium carbonate and can be sharply titrated against sodium hydroxide and phenolphthalein [0·2607 g. required 11·1 c.c. *N*/10-NaOH. Found : *M*, 234·8 (monobasic). $C_{11}H_{11}O_3NS$ requires *M*, 237]. It has no marked basic properties, dissolving in hot, concentrated hydrochloric acid and crystallising unchanged on cooling. It is soluble in acetone or glacial acetic acid, sparingly soluble in ether, and practically insoluble in benzene, ligroin, or chloroform.

The *ethyl* ester was prepared by keeping the acid (1 g.) in excess of cold, absolute alcohol, containing dry hydrogen chloride, for 24 hours; when the resulting solution was diluted, and neutralised with sodium carbonate, the *ester* separated in small, lustrous, colourless needles (0·8 g.), which, after recrystallisation from benzene–ligroin, melted at 139—140° (Found : C, 58·7; H, 5·7. $C_{13}H_{15}O_3NS$ requires C, 58·9; H, 5·7%). It is readily soluble in alcohol, ether, or benzene, and sparingly soluble in ligroin.

The ester was also obtained directly from ethyl glutaconate: A mixture of ethyl glutaconate (1 mol.) and *o*-aminothiophenol (1 mol.) was heated under reflux, in an atmosphere of carbon dioxide, at 160—180° for 3 hours; a brown gum was then obtained, from which some crystals separated on standing. The crystalline product was extracted from the gum with hot ligroin, from which it separated on cooling in small, colourless, glistening needles, m. p. 138—140°. A mixture with the ester prepared as described above melted at 139—140°.

Resolution of 4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic Acid into Optically Active Components.*—d-4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic acid.* From a solution of the *dl*-acid (4·7 g.) and anhydrous brucine (7·9 g.) in warm alcohol (60 c.c.) the brucine salt was rapidly deposited in small, soft, colourless needles. After cooling, the salt was collected and recrystallised three times from alcohol; its specific rotation then became constant. The l-*brucine* d-4-*ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetate* so obtained gave m. p. 164—165° (softening at 155°) and $[\alpha]_{5461}^{20°}$ +154·7° in aqueous solution ($l = 2$; $c = 0{\cdot}527$). On decomposition of this salt with cold, dilute hydrochloric acid, the d-*acid* was deposited in fine, colourless needles, which on recrystallisation from alcohol gave the pure *d*-acid (1 g.), m. p. 230° and $[\alpha]_{5780}^{20°}$ +436·9°, $[\alpha]_{5461}^{20°}$ +506°, $[\alpha]_{4359}^{20°}$ +981° in absolute ethyl alcohol ($l = 2$; $c = 0{\cdot}6008$) (Found: C, 56·0; H, 4·7. $C_{11}H_{11}O_3NS$ requires C, 55·7; H, 4·6%).

Ethyl d-4-*ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetate* was obtained by treating the pure *d*-acid with cold alcoholic hydrogen chloride. It separated from benzene–ligroin in short, thin, colourless needles, m. p. 145—146° and $[\alpha]_{5780}^{20°}$ +424·5°, $[\alpha]_{5461}^{20°}$ +491·7°, $[\alpha]_{4359}^{20°}$ +948·8° in absolute alcohol ($l = 2$; $c = 0{\cdot}5512$).

l-4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic acid.* The crude *l*-acid (1·7 g.), recovered from the mother-liquor of the above described brucine salt, and cinchonine (2·2 g.), were dissolved in alcohol (12 c.c.). After the addition of ether, the cinchonine salt gradually separated in small, colourless prisms, which were recrystallised twice from aqueous alcohol; m. p. 193—195° (softening at 175—180°). This salt, decomposed with cold, dilute hydrochloric acid, gave the pure l-*acid* (0·5 g.) in microscopic, colourless needles, m. p. 229—230° and $[\alpha]_{5780}^{20°}$ −435·5°, $[\alpha]_{5461}^{20°}$ −505°, $[\alpha]_{4359}^{20°}$ −976° in absolute ethyl alcohol ($l = 2$; $c = 0{\cdot}6004$).

Ethyl 3-*Keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*propionate* (I; R = $CH_2{\cdot}CO_2Et$).—This compound was synthesised for comparison with the compound obtained from *o*-aminothiophenol and glutaconic acid. It melts at 91°, whilst the isomeric ethyl ketotetrahydro-1 : 5-heptabenzthiazine-2-acetate melts at 139—140°.

o-Aminothiophenol (3·4 g.; 2 mols.) and ethyl α-bromoglutarate (3·2 g.) were heated together under reflux, in an atmosphere of carbon dioxide, at 120—130° for an hour; a brisk reaction then occurred with elimination of alcohol and formation of a crystalline material (hydrobromide). The crude product was extracted with hot ligroin, from which *ethyl* 3-*keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*propionate* separated in small, colourless, silky needles; these, after recrystallisation from ligroin, melted at 91° (Found: C, 58·8; H, 5·6. $C_{13}H_{15}O_3NS$ requires C, 58·9; H, 5·7%). The residue remaining after the extraction of the ester consisted of the hydrobromide of *oo'*-diaminodiphenyl disulphide. On hydrolysis of the ester, 3-keto-2 : 3-dihydro-1 : 4-benzthiazine-2-propionic acid was obtained in colourless needles, m. p. 174—175°.

II. *Cinnamic Acid and* o-*Aminothiophenol.*

4-*Keto*-2-*phenyltetrahydro*-1 : 5-*heptabenzthiazine* (III).—A mixture of o-aminothiophenol (8 g.) and cinnamic acid (10 g.) was heated for 2 hours under reflux, in an atmosphere of carbon dioxide, at 160—170°; a vigorous reaction then set in with elimination of water. On cooling, the product set to a hard, reddish-brown mass which, on crystallisation from alcohol, yielded 4-*keto*-2-*phenyltetrahydro*-1 : 5-*heptabenzthiazine* in short, colourless, silky needles, m. p. 177°. Yield 11 g. (Found: C, 70·5; H, 5·0. $C_{15}H_{13}ONS$ requires C, 70·6; H, 5·1%).

The compound is soluble in chloroform, acetone, or glacial acetic acid, sparingly soluble in ether or benzene, and insoluble in water. It dissolves in hot concentrated hydrochloric acid and separates from the solution unchanged on cooling.

The *acetyl* derivative (XVI; R = Ph) was obtained by boiling the substance with excess of acetic anhydride for 15 minutes. It crystallised from alcohol in short, glistening, colourless needles, m. p. 155—156° (Found: C, 68·2; H, 5·0. $C_{17}H_{15}O_2NS$ requires C, 68·7; H, 5·0%). It is readily hydrolysed by warming on the water-bath with dilute hydrochloric acid, giving the original material.

The Sulphoxide, $C_6H_4\langle^{SO\cdot CHPh}_{NH-\!-CO}\rangle CH_2$.—To a solution of the heptabenzthiazine (0·6 g.) in warm acetone (15 c.c.), a 4% solution of potassium permanganate in aqueous acetone was added until in slight excess, together with a little dilute sulphuric acid. The mixture was then boiled and filtered hot and the residue was extracted with hot acetone. The almost pure *sulphoxide* separated from the filtrate and was collected after dilution with water and cooling. It separated from acetone–alcohol or from dilute acetic

acid in clusters of thin, silky needles, m. p. 210° (Found: C, 66·4; H, 4·8. $C_{15}H_{13}O_2NS$ requires C, 66·4; H, 4·8%).

The sulphoxide is soluble in glacial acetic acid, sparingly soluble in alcohol or ether, and insoluble in water. It can also be obtained, in an almost pure condition, by treating the heptabenzthiazine with hydrogen peroxide (30%) in cold glacial acetic acid solution and diluting the mixture with water after several hours.

The Sulphone.—To a solution of the heptabenzthiazine (0·7 g.) in glacial acetic acid (10 c.c.), excess of 5% aqueous potassium permanganate (20 c.c.) was slowly added at room temperature, with stirring. The *sulphone* soon began to separate from the solution and after an hour the product was collected and recrystallised from dilute acetic acid, the solution being decolorised by charcoal. It was thus obtained in short, colourless, glistening needles, m. p. 234—235° (Found: C, 62·6; H, 4·6. $C_{15}H_{13}O_3NS$ requires C, 62·7; H, 4·5%).

The sulphone is moderately easily soluble in glacial acetic acid, sparingly soluble in alcohol or benzene, and insoluble in light petroleum, chloroform, or water. It is also formed when the heptabenzthiazine is oxidised by chromic acid in boiling glacial acetic acid solution.

Action of Alkali on 4-Keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine: Formation of o-Cinnamamidothiophenol (IV).—When the heptabenzthiazine is heated for some time with excess of dilute caustic alkali solution, complete hydrolysis takes place into cinnamic acid and *o*-aminothiophenol. When, however, it is carefully heated with a small excess of caustic alkali, the product is *o-cinnamamidothiophenol.*

4-Keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine (4 g.) was heated with 10% caustic potash solution (40 c.c.) and a little alcohol (8 c.c.) under reflux for 20—30 minutes, a deep yellow solution being obtained. After cooling, this was diluted with water and treated with carbon dioxide; *o*-cinnamamidothiophenol was then precipitated as a faintly yellowish-white, pasty mass. It crystallised from alcohol in clusters of small, almost colourless needles, m. p. 147—148°. Yield, 2 g. (Found: C, 70·6; H, 5·2. $C_{15}H_{13}ONS$ requires C, 70·6; H, 5·1%).

o-Cinnamamidothiophenol is readily soluble in acetone, chloroform, or benzene, and moderately easily soluble in ether or ligroin. It dissolves in caustic soda and slowly in sodium carbonate, giving yellow solutions, from which it is precipitated on acidification. It is readily oxidised to the corresponding disulphide by means of iodine, hydrogen peroxide or ferric chloride, or by exposure to the air.

The *mercurichloride* is precipitated when an alcoholic solution of the cinnamamidothiophenol is treated with aqueous mercuric chloride. It crystallises from alcohol, in which it is only sparingly soluble, in fine, colourless needles, m. p. 211—212°.

Conversion of o-*Cinnamamidothiophenol into* 3-*Keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine* (VI).—*o*-Cinnamamidothiophenol was heated in an atmosphere of dry carbon dioxide at 165—170° for 4—6 hours. The resulting dark, viscous liquid set, on cooling, to a hard, glassy mass, which was powdered and extracted with ether. The colourless, crystalline residue separated from alcohol in clusters of small, yellowish-white, silky needles. It proved to be 3-keto-2-benzyldihydro-1 : 4-benzthiazine and melted, alone or mixed with a specimen synthesised from α-bromo-β-phenylpropionic acid and *o*-aminothiophenol (see below), at 159—160°.

oo′-*Dicinnamamidodiphenyl Disulphide* (VIII).—(a) *From* o-*cinnamamidothiophenol.* From a solution of *o*-cinnamamidothiophenol (1 g.) in cold acetone (30 c.c.) to which excess of 30% hydrogen peroxide (2—3 c.c.) had been added, the *disulphide* soon separated as a mass of colourless, silky needles, which, after recrystallisation from acetone or glacial acetic acid, and when mixed with the pure disulphide synthesised as described below, melted at 163—164° (Found: C, 70·9; H, 4·8. $C_{30}H_{24}O_2N_2S_2$ requires C, 70·9; H, 4·7%).

(b) *From* oo′-*diaminodiphenyl disulphide* (VII). A solution of cinnamoyl chloride (2·6 g.) in dry benzene was gradually added to a solution of *oo′*-diaminodiphenyl disulphide (3·9 g.) in the same solvent. After 30 minutes, the pasty product was collected and treated with warm alcohol to remove the hydrochloride of the diaminodiphenyl disulphide, and the residue was crystallised from glacial acetic acid; pure *oo′*-dicinnamamidodiphenyl disulphide then separated in colourless, silky needles, m. p. 163—164° (Found: C, 71·0; H, 4·8%).

The disulphide is readily soluble in chloroform or hot benzene, sparingly soluble in alcohol, and insoluble in light petroleum.

Bromo-derivative. To a solution of *oo′*-dicinnamamidodiphenyl disulphide (0·5 g.) in dry chloroform (12 c.c.), a 10% solution of bromine in dry chloroform (6 c.c.) was gradually added; a colourless, pasty solid was then precipitated. After being washed with chloroform, this crystallised from acetone in small, glistening, colourless plates (0·4 g.), which darkened at 205° and melted at 213° (decomp.) (Found: C, 54·2; H, 3·6; Br, 23·8.

$$C_{30}H_{24}O_2N_2Br_2S_2$$

requires C, 53·9; H, 3·6; Br, 24·0%).

3-*Keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine* (VI).—(a) *From* α-*bromo*-β-*phenylpropionic acid.* A mixture of α-bromo-β-phenyl-

propionic acid (2·5 g.) and *o*-aminothiophenol (2 g.) was heated in an atmosphere of carbon dioxide at 125—130°; a vigorous reaction then set in and was complete after about 20 minutes. The crude product was crystallised twice from alcohol, pure *3-keto-2-benzyl-2 : 3-dihydro-1 : 4-benzthiazine* being obtained in short, colourless, silky needles, m. p. 159—160° (1·6 g.) (Found: C, 70·3; H, 5·1. $C_{13}H_{15}ONS$ requires C, 70·6; H, 5·1%). This substance is readily soluble in acetone, chloroform, benzene, or glacial acetic acid and moderately easily soluble in ligroin or ether. It is insoluble in concentrated hydrochloric acid and in dilute caustic soda solution, but it dissolves in cold, concentrated sulphuric acid to a yellow solution, from which it is precipitated unchanged by water. It does not form an acetyl derivative.

(b) *From ethyl cinnamate.* A mixture of ethyl cinnamate (3 g.) and *o*-aminothiophenol (2 g.) was heated under reflux in an atmosphere of carbon dioxide at 230—240° for 4—5 hours. The crude product was a deep red, oily liquid, which, on treatment with ether, yielded a pale yellow, crystalline solid. Recrystallised from alcohol, this separated in small, faintly yellow, silky needles, m. p. and "mixed m. p." with pure 3-keto-2-benzyldihydro-1 : 4-benzthiazine synthesised as above, 159—160° (Found: C, 70·5; H, 5·0%).

1-Styrylbenzthiazole (V).—(a) *From cinnamoyl chloride.* The condensation of cinnamoyl chloride with *o*-aminothiophenol takes place readily in cold benzene solution, but the following method, using the sodium salt of the aminothiophenol, is more satisfactory.

To a solution of *o*-aminothiophenol (1·3 g.) and sodium (0·23 g.) in absolute alcohol (12 c.c.), cinnamoyl chloride (1·6 g.) was gradually added, the mixture warmed on the water-bath for a few minutes, and the solution filtered from the precipitated sodium chloride and concentrated. On cooling, *1-styrylbenzthiazole* was deposited from the solution and on recrystallisation from alcohol it separated in short, thick, colourless prisms (1 g.), m. p. 112—113° (Found: C, 75·7; H, 4·8. $C_{15}H_{11}NS$ requires C, 75·9; H, 4·6%).

The *picrate* crystallised from alcohol, in which it is only sparingly soluble, in bright yellow platelets, m. p. 195—196°.

(b) *From 4-keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine.* The thiazine was heated at 240—260° for about an hour; water was evolved and the fused mass changed to a dark brown gum, which set to a hard solid. This was crystallised twice from alcohol (charcoal) and 1-styrylbenzthiazole was then obtained in short, colourless prisms. These, alone or mixed with the pure base obtained by method (a), melted at 112—113°. The yield was poor.

(c) *From cinnamic acid* (compare Hofmann, *Ber.*, 1880, **13**, 1235).

Cinnamic acid (2 g.) and *o*-aminothiophenol (1·8 g.) were heated together at 210—220° for about 2 hours; a dark-coloured gum was obtained which was difficult to purify. On treatment with picric acid in alcoholic solution, however, the picrate of the benzthiazole base was precipitated, and after crystallisation from alcohol (charcoal), this was obtained in bright yellow platelets (1 g.), m. p. 195—196° (Found: C, 54·3; H, 2·9. $C_{21}H_{14}O_7N_4S$ requires C, 54·1; H, 3·0%).

The base was also obtained in small yield by heating together cinnamic acid and aminothiophenol at a higher temperature and treating the crude product with alkali, according to Hofmann's method. Its formation did not readily take place below about 220°.

β-*Phenylpropionic Acid and* o-*Aminothiophenol:* 1-β-*Phenylethylbenzthiazole.*—A mixture of β-phenylpropionic acid (1 mol.) and *o*-aminothiophenol (1 mol.) was heated under reflux in an atmosphere of carbon dioxide at 160—170° for 2 hours. The crude product was heated for a short time on the water-bath with 10% caustic soda solution; the yellow oil obtained solidified on cooling, and on crystallisation from dilute alcohol it yielded 1-β-*phenylethylbenzthiazole* in lustrous, colourless platelets, m. p. 60—61° (Found: C, 75·4; H, 5·5. $C_{15}H_{13}NS$ requires C, 75·3; H, 5·4%). The base is moderately easily soluble in cold alcohol and readily soluble in ether.

The *picrate* separates from alcohol in small, bright yellow plates, m. p. 132—133°.

III. *Crotonic Acid and* o-*Aminothiophenol.*

4-*Keto*-2-*methyltetrahydro*-1 : 5-*heptabenzthiazine* (II; R = Me).—A mixture of crotonic acid (1·3 g.) and *o*-aminothiophenol (1·8 g.) was heated in an atmosphere of carbon dioxide at 165—170° for 20 minutes. A vigorous reaction then occurred and the whole set to a crystalline mass, which, recrystallised from alcohol, yielded pure 4-*keto*-2-*methyltetrahydro*-1 : 5-*heptabenzthiazine* in small, granular, colourless plates (2 g.), m. p. 205—206° (Found: C, 61·9; H, 5·6. $C_{10}H_{11}ONS$ requires C, 62·2; H, 5·7%).

The compound is soluble in glacial acetic acid, benzene, or ligroin, and sparingly soluble in ether. It crystallises from chloroform in thin needles.

The *acetyl* derivative (XVI; R = Me) was obtained by boiling the substance with excess of acetic anhydride for 10 minutes, and separated from dilute alcohol in thin, colourless, glistening needles, m. p. 93° (Found: C, 60·9; H, 5·5. $C_{12}H_{13}O_2NS$ requires C, 61·3; H, 5·5%). It is readily hydrolysed by warming on the water-bath with dilute hydrochloric acid or sodium carbonate for a short time,

giving the original material (m. p. 205—206°). It is moderately easily soluble in alcohol and readily soluble in ether.

IV. *Acrylic Acid and* o-*Aminothiophenol.*

4-Ketotetrahydro-1 : 5-heptabenzthiazine (IX).—Acrylic acid (2 g.) and *o*-aminothiophenol (3·5 g.) were heated together in an atmosphere of carbon dioxide at 125—130° for about an hour. The crystalline product was washed with ether and recrystallised from dilute alcohol, from which *4-ketotetrahydro-1 : 5-heptabenzthiazine* separated in small, lustrous, colourless needles (1·3 g.), m. p. 215—216° (Found: C, 60·5; H, 5·1. C_9H_9ONS requires C, 60·3; H, 5·0%). The compound is readily soluble in acetone or glacial acetic acid, sparingly soluble in benzene, and practically insoluble in ether, chloroform, or light petroleum.

The *acetyl* derivative (XVI; R = H) was obtained by boiling the compound with excess of acetic anhydride for 15 minutes. It crystallised from alcohol in small, colourless needles, m. p. 96—97° (Found: C, 59·8; H, 5·0; N, 6·3; S, 14·4. $C_{11}H_{11}O_2NS$ requires C, 59·7; H, 5·0; N, 6·3; S, 14·5%). It is hydrolysed by warm dilute hydrochloric acid, yielding the original material.

Synthesis of 4-Ketotetrahydro-1 : 5-heptabenzthiazine (IX) *from Acrylic Acid and* o-*Nitrothiophenol.*—The *o*-nitrothiophenol was obtained by reduction of *oo'*-dinitrodiphenyl disulphide by means of sodium sulphide (Claasz, *Ber.*, 1912, **45**, 747) and isolated from the solution by means of dilute acetic acid. It crystallised from light petroleum in pale yellow needles, m. p. 61°.

Addition of o-*nitrothiophenol to acrylic acid:* o-*Nitrophenylthiolpropionic acid* (XI). *o*-Nitrothiophenol (5·2 g.) and acrylic acid (2·4 g.) were together dissolved in dry benzene (25 c.c.) with the addition of 2—3 drops of piperidine, and the solution kept for 48 hours (compare Ruhemann, J., 1905, **87**, 17); o-*nitrophenylthiolpropionic acid* gradually separated in yellow crystals. Recrystallised from glacial acetic acid, it formed short, yellow needles (4 g.), m. p. 148—149° (Found: C, 47·7; H, 4·0. $C_9H_9O_4NS$ requires C, 47·6; H, 4·0%).

o-*Aminophenylthiolpropionic acid* (X). A mixture of *o*-nitrophenylthiolpropionic acid (4·5 g.), concentrated hydrochloric acid (15 g.), and tin (7·1 g.) was heated on the water-bath until the reduction was complete. The solution was then largely diluted with water, treated with hydrogen sulphide to precipitate the tin, and concentrated by evaporation in a vacuum. On cooling, the hydrochloride of *o*-aminophenylthiolpropionic acid separated in short, colourless needles, m. p. 173—174°, which soon became coloured on standing.

On treating the hydrochloride (1·2 g.) in concentrated aqueous solution with *N*-sodium hydroxide (5 c.c.), the *amino-acid* was obtained in colourless crystals (0·8 g.), which separated from dilute alcohol in short, thick needles, m. p. 87—88° (Found: C, 54·8; H, 5·7. $C_9H_{11}O_2NS$ requires C, 54·8; H, 5·6%) (compare Mayer and Horst, *loc. cit.*).

4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine.* The hydrochloride of *o*-aminophenylthiolpropionic acid (1·5 g.) was heated at 180—190° for ½ hour, hydrogen chloride and water being eliminated. On cooling, the product set to a reddish-brown solid, which, crystallised from alcohol, yielded pure ketotetrahydro-1 : 5-heptabenzthiazine (0·2 g.) in lustrous, colourless needles, m. p. and "mixed m. p." with the lactam synthesised from acrylic acid and *o*-aminothiophenol, 215—216°.

The acetyl derivative of the lactam was obtained on heating the above hydrochloride with excess of acetic anhydride for 30 minutes.

V. *Maleic Acid and* o-*Aminothiophenol.*

3-*Keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic Acid* (XIV).—Maleic acid (3·5 g.) and *o*-aminothiophenol (3 g.), when mixed, reacted readily with considerable development of heat and the whole soon set to a hard mass. After being heated for a few minutes at 100—110°, the product was crystallised from dilute alcohol, from which it separated in small, colourless needles, melting at 195—196°, and at the same temperature after mixture with pure 3-*keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic acid* synthesised from *o*-aminothiophenol and monobromosuccinic acid (see below). Yield 5 g. (93·5%) (Found: C, 53·6; H, 4·0. $C_{10}H_9O_3NS$ requires C, 53·8; H, 4·0%).

The compound is soluble in alcohol, sparingly soluble in ether, and practically insoluble in benzene, chloroform, or ligroin. It crystallises from water in thin, silky needles. It dissolves readily in cold, dilute sodium carbonate solution and is precipitated on acidification. After boiling for some time with 10% caustic potash solution it was precipitated unchanged on acidification.

The same product was obtained from fumaric acid and *o*-aminothiophenol. In this case no reaction appeared to take place in the cold, but the compound was readily formed on heating the two substances together at 150—160° for 15 minutes.

3-*Keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic Acid from Monobromosuccinic Acid.*—Monobromosuccinic acid (1 g.) and *o*-aminothiophenol (0·6 g.) were heated together in an atmosphere of carbon dioxide at 120—125° for 15 minutes; a vigorous reaction then occurred and the mixture soon set to a solid mass. The product

was crystallised twice from dilute alcohol (charcoal) and pure keto-dihydrobenzthiazineacetic acid was thus obtained in small, colourless needles (0·6 g.), m. p. 195—196° (Found: C, 54·2; H, 4·0%).

The following work was kindly carried out by Mr. G. E. WATTS:

Diacetyl Derivative of o-*Aminothioanisole.*—*o*-Aminothioanisole (10 g.) was boiled with acetic anhydride (30 g.; 4 mols.) for an hour. The resulting solution was distilled in a vacuum to remove acetic acid and anhydride, and the residual gum crystallised from alcohol, from which the *diacetyl* derivative separated in colourless, transparent prisms, m. p. 69—70°. Yield, 13 g. (82%) (Found: C, 59·1; H, 5·9; N, 6·1. $C_{11}H_{13}O_2NS$ requires C, 59·2; H, 5·8; N, 6·3%).

Preparation of Benzthiazolone (XVIII).—*Ethyl* o-*nitrophenylthiolformate*, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}CO_2Et$. To a solution (deep red) of *o*-nitrothiophenol (31 g.) in alcoholic sodium hydroxide (8 g. of NaOH in 30 c.c. of alcohol) a solution of ethyl chloroformate (21·7 g.) in alcohol (20 c.c.) was added, with shaking; the red colour of the nitrothiophenol soon disappeared, considerable heat was evolved, and sodium chloride was precipitated. The mixture was poured into water (500 c.c.) and the ethyl nitrophenylthiolformate, which separated as a yellow oil, was extracted with ether. It decomposed when heated in a vacuum.

Ethyl o-*aminophenylthiolformate.* Crude ethyl nitrophenylthiolformate (35 g.), mixed with alcohol (20 c.c.), was shaken with a solution of stannous chloride (115 g.) in concentrated hydrochloric acid (50 c.c.) for an hour, the mixture being cooled in ice from time to time. The solution was diluted, freed from tin by means of hydrogen sulphide, made alkaline with sodium bicarbonate, and extracted with ether. On removal of the ether the amino-ester remained as a colourless oil. Yield, 20 g. (67%).

The *hydrochloride* of the amino-ester was prepared by treating an alcoholic solution of the ester with hydrogen chloride and precipitated by the addition of ether. It crystallised from alcohol–ether in fine, colourless needles, m. p. 120—122° (Found: Cl, 15·2. $C_9H_{12}O_2NClS$ requires Cl, 15·2%).

Benzthiazolone. Ethyl *o*-aminophenylthiolformate, mixed with a little of its hydrochloride, was heated at 115° for 2 hours; it then changed to a crystalline mass. This, recrystallised from aqueous alcohol, gave colourless needles of benzthiazolone; they melted at 128° and were readily soluble in strong alkalis and in strong mineral acids (compare Claasz, *Ber.*, 1912, **45**, 1029).

The acetyl derivative was obtained by boiling the substance with excess of acetic anhydride for 15 minutes. It separated from aqueous alcohol in fine, colourless needles, m. p. 50° (compare Claasz,

loc. cit.), and was readily hydrolysed by warm 10% sodium hydroxide solution, giving the original material.

One of us (J. B. W.) wishes to express his indebtedness to the Chemical Society for a grant which defrayed part of the cost of this investigation.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, August 25th*, 1927.]

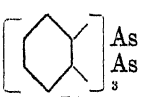
CCCLXVI.—*Organic Compounds of Arsenic. Part III. Tri-o-phenylenediarsine.*

By NIAL PATRICK MCCLELAND and JAMES BELL WHITWORTH.

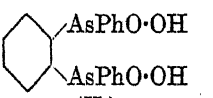
TRI-*o*-PHENYLENEDIARSINE (I) appears to be the first compound in which it is established that a pair of atoms is linked to each of three benzene rings in the ortho-position in such a way that, a symmetrical grouping being assumed, the planes of the rings are inclined at 120° to one another.

A substance, $C_{18}H_{12}N_2$, described in the literature as triphenylenediamine was obtained by von Dechend and Wichelhaus (*Ber.*, 1875, **8**, 1609) by the action of nitrobenzene on aniline or diphenylamine, but its constitution is unknown.

The new substance (I) was obtained as follows: Diazotised *o*-aminodiphenylarsinic acid coupled with phenylarsine oxide to give *phenylene*-1 : 2-*diphenylarsinic acid* (II), which was then reduced with phosphorus trichloride, presumably to phenylene-1 : 2-diphenylchloroarsine; this was not obtained in the pure state and on distillation it gave *tri*-o-*phenylenediarsine* (I), evidently by the loss of two molecules of hydrogen chloride and consequent double ring closure.



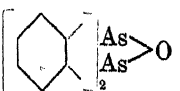
(I.)



(II.)



(III.)



(IV.)

The constitution of the substance (I) is supported by the following observations, which show that triphenylenediarsine bears the same relation to the derivatives of arsanthrene (Kalb, *Annalen*, 1921, **423**, 39) as the triarylarsines do to those of the diarylarsines: (1) as triphenylarsine dichloride decomposes on distillation into diphenylchloroarsine and chlorobenzene (La Coste and Michaelis, *Annalen*, 1880, **201**, 242; Michaelis, *ibid.*, 1902, **321**, 142, 160; Winmill, J., 1912, **101**, 720), so triphenylenediarsine tetrabromide (III) on

heating gives (in addition to bromine and triphenylenediarsine) *o*-dibromobenzene and arsanthrene bromide; (2) as di-*p*-tolylarsenious oxide on heating gives tri-*p*-tolylarsine (La Coste, *Annalen*, 1881, **208**, 20), so arsanthrene oxide (IV) on distillation gives triphenylenediarsine and arsenious oxide as indicated by the equation 3 (IV) = 2 (I) + As_2O_3 (compare the decomposition of phenylarsine oxide into triphenylarsine and arsenious oxide on heating; La Coste and Michaelis, *ibid.*, p. 239).

Moreover, the substance behaves as a tertiary arsine, being converted into the oxide by nitric acid and forming a tetrabromide and a mercurichloride.

Triphenylenediarsine is formed in the preparation of arsanthrene chloride by Kalb's method (*loc. cit.*) and probably accounts for the sparingly soluble impurity which he found in arsanthrene oxide.

The stereochemistry of the new system is under investigation, and it is hoped to prepare corresponding compounds with other elements in place of arsenic.

EXPERIMENTAL.

Phenylene-1 : 2-*diphenylarsinic Acid* (II).—Into a well-stirred, diazotised solution of *o*-aminodiphenylarsinic acid (20 g.; concentrated hydrochloric acid, 58 c.c.; water, 700 c.c.; ice, 500 g.) was run a solution of phenyldichloroarsine (18 g.) in 5*N*-caustic soda (64 c.c.) to which sodium acetate (58 g.), dissolved in ice-water (450 c.c.), had been added just previously. The mixture was made alkaline with caustic soda, boiled with charcoal, and filtered. On acidification, the filtrate gave a yellowish-brown, pasty precipitate. This was boiled with alcohol, which removed most of the coloured impurity, the residue was dissolved in a large volume of dilute aqueous ammonia, the solution neutralised with acetic acid and boiled with charcoal, and an excess of dilute acetic acid added to the boiling filtered solution; *phenylene*-1 : 2-*diphenylarsinic acid* (9 g.) then slowly separated in pale yellow, microscopic crystals which did not melt below 310° and were insoluble in water and in the usual organic solvents (Found: C, 49·0; H, 3·5. $C_{18}H_{16}O_4As_2$ requires C, 48·4; H, 3·6%).

Tri-o-*phenylenediarsine* (I).—Phenylene-1 : 2-diphenylarsinic acid (9 g.), suspended in chloroform (100 c.c.), was treated with excess of phosphorus trichloride (25 g.), heat being evolved and most of the acid dissolving. The solution was heated on the water-bath for 3 hours and filtered from a little tar. On distillation of the solvent a dark brown, oily residue was obtained from which no crystalline product could be isolated. It was therefore heated under reduced pressure; vigorous frothing occurred at 120—300°,

and at 320—340°, crystals of *triphenylenediarsine* gradually sublimed on the upper part of the distilling flask, but no distillate was obtained. The crystalline product was collected and a further quantity was obtained on extracting the charred residue in the flask with hot benzene. On recrystallisation from benzene (charcoal), triphenylenediarsine (2·5 g.) was obtained in small, almost colourless plates, m. p. 295—296°. It is soluble in benzene, acetone, or light petroleum, readily soluble in chloroform, sparingly soluble in alcohol or ether, and insoluble in water. It can be sublimed without decomposition (Found: C, 57·4; H, 3·2; As, 40·1; *M*, in camphor by Rast's method, 360, 396, 364. $C_{18}H_{12}As_2$ requires C, 57·1; H, 3·2; As, 39·8%; *M*, 378).

The authors are indebted to Professor Hutchinson for the determination of the crystallographic constants:

System: Monoclinic (holohedral). $a : b : c = 1·589 : 1 : -$; $\beta = 113° 15'$. Forms present: *a*(100), *c*(001), *m*(110). Angles observed: *am* 55° 35′, *ac* 66° 45′.

The crystals are elongated parallel to the axis of the zone [*am*] and are either tabular parallel to *a* with *m* and *c* small or bounded by *m* and *c* planes with *a* small or absent. The face *c* is invariably somewhat rounded. The optic axial plane is perpendicular to the plane of symmetry and lies in the obtuse axial angle. A negative acute bisectrix emerges obliquely from *a*. On viewing the crystal in monochromatic convergent light perpendicular to a pair of *m* faces, the emergence of an optic axis near the edge of the field can be seen. In white light, the dark brush passing through the centre of the ring system is replaced by brilliant red and blue fringes, indicating strong dispersion, and no extinction can be obtained on the *m* face in parallel light. The material available did not lend itself to an accurate determination of the optical constants, but β for sodium light was found to be 1·790 approximately.

The *mercurichloride* was obtained in short, colourless needles from the diarsine and mercuric chloride in cold acetone; after recrystallisation from alcohol, in which it was sparingly soluble, it melted at 285—286°. It was readily decomposed by warm dilute caustic soda solution.

The *oxide* was obtained on boiling the diarsine with concentrated nitric acid and pouring the resulting solution into water. It was readily soluble in alcohol and separated from dilute aqueous alcohol in short, thin, colourless needles, which did not melt below 360° (Found: C, 52·6; H, 3·0. $C_{18}H_{12}O_2As_2$ requires C, 52·7; H, 2·9%).

The *tetrabromide* (III) was precipitated as an orange-red, crystalline substance, m. p. 255—256°, when the diarsine was treated with a small excess of bromine in dry chloroform (Found: Br, 45·7.

$C_{18}H_{12}Br_4As_2$ requires Br, 45·9%). It is readily soluble in acetone or alcohol and in hot glacial acetic acid (with decomp.), sparingly soluble in chloroform, and insoluble in ether, benzene, or light petroleum. It is readily decomposed by dilute caustic soda solution or even by water, giving the colourless oxide (Found: As, 36·4. Calc. for $C_{18}H_{12}O_2As_2$: As, 36·7%).

When the tetrabromide was heated under reduced pressure (15 mm.), decomposition took place at about 260°, much bromine was evolved, and a small quantity of a yellow liquid distilled; the residue set to a crystalline mass on cooling. The liquid product was dissolved in ether, treated with caustic soda to remove free bromine, and distilled in a vacuum, being thus obtained as a colourless oil, b. p. 104—105°/15 mm., 224°/ordinary pressure (Found: Br, 68·2. Calc. for $C_6H_4Br_2$: Br, 67·8%). On intensive cooling, the liquid set to a colourless solid, m. p. 4°. It was concluded that the liquid was *o*-dibromobenzene, which has b. p. 224° and m. p. 5·6°. (The *m*-isomeride has b. p. 220° and m. p. — 7°, and the *p*-isomeride, m. p. 87°.)

As it would probably have been difficult to separate the small amount of arsanthrene bromide from the triphenylenediarsine by recrystallisation, the crystalline residue was treated with alcoholic ammonia to convert the arsanthrene bromide into the oxide. After dilution with water, the product was collected and extracted with hot alcohol, the portion remaining undissolved consisting of triphenylenediarsine, which after recrystallisation from benzene gave m. p. and "mixed m. p." 295—296°. The cooled alcoholic extract was filtered from a small amount of the diarsine which had separated and was then concentrated. Arsanthrene oxide, which separated on cooling, crystallised from alcohol in small, lustrous plates which, alone or mixed with pure arsanthrene oxide, melted at 194—195°.

The presence of bromide in the ammoniacal liquor was verified.

Treatment of triphenylenediarsine with chlorine yielded a light yellow compound, which has not been investigated. Methyl iodide gave no addition compound on prolonged heating with the diarsine in a sealed tube at 50—60°.

Formation of Triphenylenediarsine from Arsanthrene Oxide.—Pure arsanthrene oxide distilled under 15 mm. pressure, without appreciable decomposition, as a yellow liquid, which rapidly solidified. When, however, the pure oxide was distilled in a current of carbon dioxide under only slightly reduced pressure, considerable decomposition took place. Arsenious oxide sublimed into the receiver, and a crystalline substance on the upper part of the distilling flask. The crystalline product was extracted with hot alcohol to remove any unchanged oxide and then recrystallised from

benzene, from which it separated in small, colourless plates, m. p. 295—296°, and at the same temperature after mixture with pure triphenylenediarsine. The dark brown residue in the distilling flask gave a further small quantity of the diarsine on extraction with benzene.

Triphenylenediarsine appears to be formed during the distillation of arsanthrene chloride, for, when arsanthrene chloride prepared by Kalb's method (*loc. cit.*) was converted into the oxide by alcoholic ammonia, and the oxide crystallised from alcohol, a small quantity of triphenylenediarsine remained undissolved. It separated from benzene in small, colourless plates, m. p. and "mixed m. p." with the pure diarsine 295—296° (Found: C, 57·3; H, 3·1%), and on oxidation with nitric acid it gave triphenylenediarsine oxide as fine needles (Found: C, 52·7; H, 2·8%).

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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CCCLXVII.—*The Halogenation of Phenols. Part II. Iodination.*

By FREDERICK GEORGE SOPER and GILBERT FREEMAN SMITH.

THE relative ionisation constants of chlorine and hypochlorous acid to give a positive halogen ion (Soper and Smith, J., 1926, 1582) express qualitatively the ease with which these substances chlorinate phenols. A study of the chlorination by hypochlorous acid showed, however, that the hypochlorous acid *molecule* was the chlorinating agent, so that the parallelism between the ease of chlorination and the ionisation constant of the chlorinating molecule is not due to preliminary ionisation into a reactive positive halogen ion. The ionisation constant of the halogenating agent may be regarded as a measure of the number of polarised molecules present and collisions between these and other molecules may be effective. It was of interest to extend this line of argument to iodination by iodine and by hypoiodous acid, the relative ionisation constants of which, given by the ratio K_h/K_w (K_h being the hydrolysis constant, $C_H.C_I C_{HOI}/C_{I_2} = 3 \times 10^{-13}$, of iodine in water; Bray and Connolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485), are as 30 to 1. It might be expected from this ratio that the ease of halogenation by iodine would be comparable with that by hypoiodous acid.

The mechanism of the iodination of phenols was investigated by Cofman (J., 1919, **115**, 1040), who showed that in acid solution iodine does not iodinate, whilst the active iodine in an alkaline

solution was equal to the concentration of hypoiodous acid, as calculated from the known kinetics of iodate formation (Skrabal, *Monatsh.*, 1911, **32**, 171). It might appear from these facts that iodine is incapable of iodination and that hypoiodous acid or (as Cofman suggests as an alternative) the positive iodine ion is the halogenating agent. As, however, in acid solution the phenol would be mainly un-ionised, whilst in alkaline solution the very much more highly reactive phenoxide ions would be present, the mechanism has been further examined in order to determine whether iodine is capable of reacting with phenoxide ions.

Examination of the speed of iodination of phenol was carried out by the use of a solution of iodine in potassium iodide in the presence of a neutral phosphate buffer. If molecular iodine is involved in the interaction, then the speed will be proportional, on the classical reaction-velocity equation, to the concentration of free iodine in the mixture. The equilibrium concentration of free iodine can be calculated from the expression $C_{I_2}C_{I'}/C_{I_3'} = K_1$ (Bray and MacKay, *J. Amer. Chem. Soc.*, 1910, **32**, 914), using the appropriate value for K_1 which depends on the iodide concentration. The speed of iodination at constant phenol concentration will thus be given by $v = k_{I_2}K_1C_{I_3'}/C_{I'}$, and since, in the presence of excess of iodide ions, $C_{I_3'}$ is represented sufficiently accurately by the thiosulphate titre of the solution, the velocity coefficient, k_1, of the reaction calculated from the equation

$$v = k_1 \times \text{thiosulphate titre} \quad . \quad . \quad . \quad . \quad (1)$$

should vary inversely as the iodide-ion concentration.

If the iodination is caused by hypoiodous acid, the velocity coefficient k_1 should vary approximately as the inverse of the square of the concentration of the iodide ion at constant hydrogen-ion concentration, for $C_{HOI}a_{H^+}.a_{I'}/C_{I_3} = K_h = 3 \times 10^{-13}$, a denoting the appropriate activity * of the ion, and hence

$$v = k_{HOI} \cdot C_{HOI} = k_{HOI}K_hK_1C_{I_3'}/a_{H^+}.a_{I'}C_{I'} \quad . \quad . \quad . \quad (2)$$

The results obtained are given in Table I. The values of the activity of the iodide ion, $a_{I'}$, have been interpolated for the appropriate ionic strength, μ, from a table of the activities of the chloride ion (Lewis and Randall, " Thermodynamics," 1924, p. 351). The concentrations of iodine and of hypoiodous acid given in cols. 4 and 6, respectively, are the initial equilibrium concentrations of these substances in the reaction mixture. The unimolecular coefficient k_1 (the mean of two experiments agreeing to within 1%) is seen to

* The activity of a neutral molecule has been equated to its concentration, in the absence of other information.

be proportional to the initial concentration of the hypoiodous acid. Although the concentration of the iodine is between 10^4 and 10^5 times that of the hypoiodous acid, there is no appreciable iodination by iodine.

TABLE I.

Ph·OH = 0·010; I_2 added = 0·001M; Temp. = 25·0°; $a_{H^+} = 10^{-7}$.

μ.	$C_{I'}$.	$K_1 . 10^3$.	$C_{I_2} . 10^5$.	$a_{I'}$.	$C_{HOI} . 10^{10}$.	k_1.	$\frac{10^{-4} . k_1}{C_{I_2}}$.	$\frac{10^{-8} . k_1}{C_{HOI}}$.
0·2092	0·1	1·31	1·295	0·0745	5·231	0·1926	1·486	3·685
0·3092	0·2	1·21	0·605	0·1434	1·287	0·0477	0·788	3·75
0·5092	0·4	1·00	0·250	0·2724	0·2752	0·0102	0·407	3·71

It is now necessary to differentiate between the interaction of hypoiodous acid and that of positive iodine ion with the phenol molecule or with the phenoxide ion. This is possible by an examination of the speed of iodination in solutions containing a constant concentration of iodide ion and various hydrogen-ion concentrations. Since the reaction is examined over the hydrogen-ion concentration range from $0·5 \times 10^{-7}$ to 4×10^{-7}, the phenol exists mainly in the un-ionised condition, its ionisation constant, K_a, being $1·1 \times 10^{-10}$. The concentration of phenoxide ions is thus inversely proportional to the hydrogen-ion concentration.

For a reaction between hypoiodous acid and phenol, the speed will be given by

$$v = k_2 C_{HOI} C_{Ph·OH} = k_2 K_1 K_h C_{Ph·OH} C_{I_3'}/a_{H^+} a_{I'} C_{I'}$$
$$= k_2 K_I K_h C_{Ph·OH} C_{I_3'}/a_{H^+} f_{I'} C_{I'}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $f_{I'}$ is the activity coefficient of the iodide ion. The velocity coefficient, k_1, of equation (1) should vary inversely as $f_{I'} a_{H^+}$, or, since the ionic strength is nearly constant in the different mixtures, inversely as the hydrogen-ion activity. If the reaction is between the phenoxide *ion* and hypoiodous acid,

$$v = k_3 C_{HOI} C_{Ph·O'}$$
$$= k_3 K_1 K_h K_a C_{Ph·OH} C_{I_3'}/a_{H^+}^2 f_{Ph·O'} f_{I'} C_{I'}^2 \quad . \quad . \quad (4)$$

and k_1 should vary approximately as the inverse of the square of the hydrogen-ion activity.

For iodination by positive iodine ions, the concentration of which is controlled by the equilibrium constant $K_2 = a_{I^+} a_{I'}/C_{I_2} = a_{I^+} C_{I'} f_{I'}/C_{I_2}$, the velocity equation will be $v = k_4 C_{Ph·OH} C_{I^+} = k_4 K_1 K_2 C_{Ph·OH} C_{I_3'}/C_{I'} a_{I'} f_{I'}$, and k_1 would be independent of the hydrogen-ion concentration, whilst for an interaction of positive iodine ion with the phenoxide ion the constant k_1 would be inversely proportional (approximately) to the hydrogen-ion concentration. Actually, experiments carried out at the hydrogen-ion

activities of 0·5, 1·0, 2·0, and 3·98 × 10^{-7} showed that the velocity coefficient k_1 varied more rapidly than the inverse of the hydrogen-ion activity of the mixture, but less rapidly than its inverse square. The results are summarised in Table II.

TABLE II.

Ph·OH = 0·010; KI = 0·100; temp. = 25·0°.

HPO_4''.	H_2PO_4'.	μ.	$f_{I'}$.	a_{H^+}. 10^7.	k_1 (obs.).	$10^7 \times k_1 a_{H^+}$.	$10^{14} \times k_1 a_{H^+}^2$.	k_1 (calc.).
0·0370	0·0130	0·224	0·741	0·5	0·420	0·210	0·105	0·440
0·0296	0·02037	0·209	0·745	1·0	0·193	0·198	0·193	0·182
0·0205	0·0295	0·191	0·752	2·0	0·083	0·166	0·322	0·081
0·0126	0·0374	0·175	0·759	3·98	0·036	0·143	0·570	0·038

Assigning the values 4·85 × 10^9 and 2·76 × 10^7 to k_3 and k_2 respectively, and taking the value of $f_{Ph\cdot O'}$ as equal to that of $f_{I'}$, k_1 has been calculated from the equation

$$v = k_2 C_{HOI} C_{Ph\cdot OH} + k_3 C_{HOI} C_{Ph\cdot O'}$$
$$= \frac{K_1 K_h C_{Ph\cdot OH} C_{I_2'}}{a_{H^+} \cdot C_{I'}^2 f_{I'}} (k_2 + k_3 K_a / a_{H^+} f_{Ph\cdot O'}) \quad . \quad . \quad . \quad (5)$$

which, in combination with (1), gives

$$k_1 = \frac{K_1 K_h C_{Ph\cdot OH}}{a_{H^+} \cdot C_{I'}^2 f_{I'}} (k_2 + k_3 K_a / a_{H^+} f_{Ph\cdot O'}) \quad . \quad . \quad . \quad (6)$$

Bearing in mind the necessarily approximate values used for the activities of the various ions and neutral molecules, the divergencies between the observed and calculated values of k_1 are not unreasonable.

Conclusions.

It would thus appear that the iodination of phenol is not caused by the positive iodine ion, but that the main reactions are those between the hypoiodous acid and the ionised and un-ionised phenol, the reactivity of the phenoxide ion being 180 times that of the phenol molecule. Molecular iodine is a singularly poor iodinating agent, being at least 10^6 times less active than hypoiodous acid in spite of its greater ease of ionisation and, presumably, its more highly polar condition.

The behaviour of halogens and the hypohalous acids towards phenols (as illustrated by chlorine and iodine) is thus not entirely explained on a theory of reactivity governed by the polar state of the molecules, iodination indicating that some other factor can dominate. This factor may be the affinity of the residual nuclear hydrogen for the residue of the halogenating molecule. The affinity of the hydrogen ion for the hydroxyl ion is so much greater than for the iodide ion that hypoiodous acid becomes very much

more reactive than iodine. In chlorination, however, the large difference in the affinities of Cl· for OH′ and for Cl′ ($4{\cdot}8 \times 10^{10}$ to 1) appears to be the controlling factor.

EXPERIMENTAL.

Buffer Solutions.—The phosphate buffer solutions were prepared from potassium dihydrogen phosphate (B.D.H., A.R.) and sodium hydroxide free from carbonate; the quantities taken (Table II) were interpolated from those given by Clark ("Determination of Hydrogen Ions," N.Y., 1920, p. 76). Conductivity water was used in making up all the solutions.

Measurement of the Speed of Iodination.—The reaction was started by addition of the iodine solution in potassium iodide to the mixture of phenol (m. p. 40·0°) and phosphate buffer solution at 25·0°. 10 C.c. of the reaction mixture were removed at suitable intervals and run into 50 c.c. of 0·5*N*-sulphuric acid, whereby the reaction was stopped. Titration of the residual iodine with *N*/500-thiosulphate was carried out in an atmosphere of nitrogen, which enabled perfectly sharp end-points to be obtained. The results for a typical experiment are given in Table III.

TABLE III.

0·05*M*-KH_2PO_4; 0·0296*M*-NaOH; 0·01*M*-Ph·OH; 0·001*M*-I_2; temp. 25·0° ± 0·02°.

Time (mins.) .	0	8·70	13·97	22·80	35·58	49·90	64·93
$[I_3'] \times 10_4$ ...	9·67	8·07	7·27	5·98	4·60	3·48	2·56
$k_1/2{\cdot}303$	—	0·0208	0·0205	0·0210	0·0208	0·0205	0·0205

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

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CCCLXVIII.—*The Activity Theory of Reaction Velocity. The Interaction of* N-*Chloroacetanilide and Hydrochloric Acid.*

By FREDERICK GEORGE SOPER and DAVID REGINALD PRYDE.

THE effect of electrolytes on the speed of reactions catalysed by acids is interpreted at the present time along two lines. On one theory, the catalyst is the hydrogen ion, its catalytic activity being proportional either to its thermodynamic activity (Harned, *J. Amer. Chem. Soc.*, 1918, **40**, 1461), which is affected by the presence of salts, or to its concentration (Brönsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185) as calculated from the concentration ionisation constant, which changes with the ionic strength (Arrhenius,

Z. physikal. Chem., 1899, **31**, 197; Brönsted, J., 1921, **119**, 574). The other theory, which has recently been extended by Dawson (Dawson and Carter, J., 1926, 2282 *et seq.*), attributes catalytic activities to the undissociated molecule and to the acid anion, as well as to the hydrogen ion. On the latter theory, the catalytic activities of the various ions are assumed to be proportional to their concentrations. It may be noted, however, that Dawson, in calculating his hydrogen-ion concentrations in acetic acid–acetate mixtures, uses a constant value for the ionisation constant of acetic acid in which he substitutes for the acid and anion concentrations (Dawson and Dean, *ibid.*, p. 2876); no allowance is made for the increase of the concentration ionisation constant (some 200%: Brönsted, *loc. cit.*; compare K_w, Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 930) as the salt concentration is increased from 0 to 1·0*N*.

A factor very generally neglected in the study of acid catalysis is the effect the electrolyte may have on the active mass of the non-electrolyte, as demonstrated by the experiments of Jones and Lapworth (J., 1911, **99**, 1427), who found that the equilibrium constant of the reaction $EtOH + CH_3{\cdot}CO_2H \rightleftharpoons CH_3{\cdot}CO_2Et + H_2O$ changes by more than 100% as the amount of the catalyst, hydrogen chloride, is altered. Since the catalyst does not appear in the equilibrium constant, the velocity coefficients k and k' in the equations, $v = kC_{catalyst}C_{alcohol}C_{acid}$ and $v' = k'C_{catalyst}C_{ester}C_{water}$, must vary as the catalyst concentration changes. The general procedure has been to regard k as strictly constant, and to deduce the effective concentration of the catalyst on this assumption. It is obvious that this procedure may lead to erroneous theories. If deductions are to be made as to the effective concentrations of the catalyst, k, and therefore k/k', must be strictly constant. The equilibrium constant of a system must therefore be expressed in such a way as to be independent of the changes in medium caused by the addition of neutral salts, and the velocity equation must be modified so as to be in harmony with this equilibrium constant. An equilibrium constant of this nature was proposed by van 't Hoff (Lectures, 1898), concentrations being replaced by the ratio of concentration to the limiting solubility in the particular medium. Replacement of concentrations by this ratio in the velocity equation $v = kC$ gives $v = k_0C/S$; Dimroth (*Annalen*, 1910, **377**, 127) used this equation in studying the effects of solvents on the velocity of intramolecular transformation, and found that, whilst the classical velocity coefficient had values which differed as much as 100-fold from each other, the values of k_0 only exhibited a 3-fold variation. It would thus appear that part of the effect of the medium on

reaction speed is connected with solubility. It follows that, if the solubility of a non-electrolyte, such as ethyl acetate, is decreased by the presence of electrolytes, its reactivity may be increased. This is also indicated from a consideration of the kinetic equilibrium of a solid with its saturated solution. If the solubility is decreased, a greater proportion of the solute molecules must possess sufficient translational energy to deposit themselves on the surface of the solid, and the reactivity, which depends on the proportion of molecules having an energy greater than some critical value (Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226; Hinshelwood, *Phil. Mag.*, 1925, **2**, 360), may be expected to increase (Scatchard, *J. Amer. Chem. Soc.*, 1923, **45**, 1581).

The van 't Hoff equilibrium constant is a partial statement of the activity constant. Defining the activity, a_A, of a substance A by the expression $F_A = C_A + RT \log a_A$, where F_A is the partial free energy and C_A is a constant, and putting $F_A + F_B = F_P + F_Q$ as the condition * of equilibrium in the system $A + B \rightleftharpoons P + Q$, it is seen that $a_A a_B / a_P a_Q$ is constant and independent of the medium. The modified velocity equation corresponding to the classical equation is thus $v = k a_A a_B$, but it is important to note that this equation is only one of a number which, when applied to a balanced reaction, satisfy the activity equilibrium constant. The general velocity equation is of the type

$$v = k_0 a_A a_B F_1 \text{ (activities)}. \quad F_2 \text{ (specific effect of solvent)}. \quad F_3 \ldots F_n, \ldots \ldots \ldots \ldots \ldots \ldots \quad (1)$$

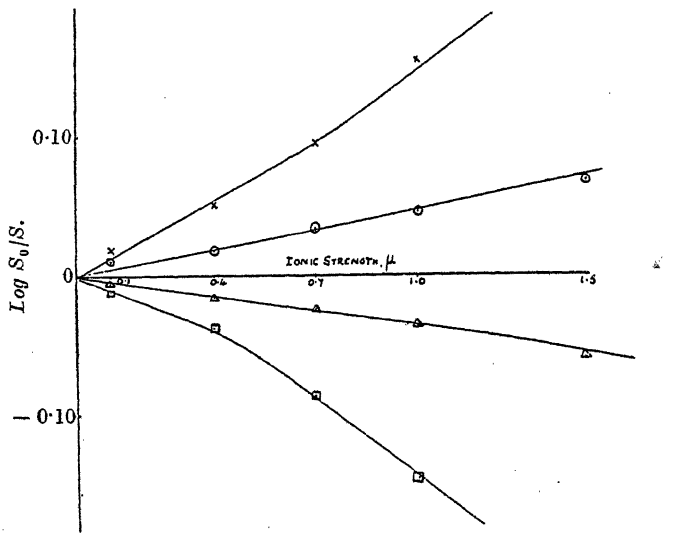
with the stipulation that the functions F_1, F_2 . . ., should be common to both the forward and the reverse reactions of the reversible change.

The object of the present work was to test the equation $v = k a_A a_B$, or, if this was inadequate, some equation of the general type (1), and for this purpose a knowledge of the activities of the reacting substances in the presence of each other is necessary. Whilst the effect of small concentrations of a non-electrolyte on the activity of an electrolyte is negligible, the electrolyte may exert a large effect on that of the non-electrolyte. The determination of the activity of a substance in the presence of those reagents which are causing its decomposition is difficult, and it does not suffice to regard the salting-out effect of all electrolytes as identical at equivalent concentrations. It has been possible to overcome this difficulty in the study of the interaction of hydrochloric acid and *N*-chloroacetanilide (Orton and Jones, *Rep. Brit. Assoc.*, 1910,

* This is permissible if a displacement of the equilibrium is not attended by a change in the ionic strength (Soper, *J. Physical Chem.*, 1927, **31**, Nov.).

85; Rivett, *Z. physikal. Chem.*, 1913, **82**, 301; Harned and Seltz, *J. Amer. Chem. Soc.*, 1922, **44**, 1475), for both hydrogen and chlorine ions must be present before the *N*-chloroacetanilide reacts, and it was therefore possible to measure separately the effects of these ions on the activity of the chloroamine. It was found that the replacement of the chloride ion by the nitrate ion raised the solubility of the chloroamine in a certain ratio, which depended on the salt concentration, but was otherwise independent of the kation present. From the solubility in nitric acid, that in hydrochloric acid could be deduced, and the activity coefficient was found in

FIG. 1.



△ HCl, ⊡ HNO_3, × KCl, ⊙ KNO_3 *solutions.*

this way to change by 13% over the hydrochloric acid range examined (0·1—1·5*M*). The results are given graphically in Fig. 1, where the logarithm of the activity coefficient of the chloroamine (the ratio of the solubility in water to that in the salt solution) has been plotted against the ionic strength.

Measurement of the Rate of Interaction of Hydrochloric Acid and N-*Chloroacetanilide.*—The transformation of *N*-chloroacetanilide to *o*- and *p*-chloroacetanilides was shown by Orton and Jones (*loc. cit.*) to involve two successive stages: first, an interaction of the hydrochloric acid and the chloroamine with the production of chlorine, and secondly, reaction between the chlorine and the acetanilide. It has since been shown by one of us (*J. Physical Chem.*, 1927, **31**, 1192) that the speed of the transformation is

approximately equal to that of the first stage, but that the measurement of the rate of reaction is complicated by simultaneous *N*-chlorination of the chloroanilides which are produced. The effect of this was shown to be that the rates of the transformation as ordinarily measured indicate an apparent reactivity of the hydrochloric acid, which is too great in the more concentrated acid solutions. In order to measure the true rate at which chlorine is being formed, it is necessary to have present excess of some substance which is readily chlorinated and does not itself react with the hydrochloric acid or the chloroamine. Acetanilide, phenol, and *p*-cresol have been used for this purpose, and have given identical results.

It is possible that chlorine may be produced from a chloroamine by two mechanisms: (1) a direct interaction of hydrochloric acid and the chloroamine the rate of which it is desired to measure, and (2) a primary hydrolysis of the chloroamine to hypochlorous acid, followed by the rapid interaction of hydrochloric and hypochlorous acids, giving chlorine (k_2 at $25° = 1{\cdot}0 \times 10^6$; Soper and Smith, J., 1926, 1582). If (2) occurs appreciably, the rate of chlorine formation will be greater than the rate of interaction of the chloroamine and hydrochloric acid. In aqueous solution, the rate of hydrolysis of *N*-chloroacetanilide is very slow, for in the presence of phenols with which hypochlorous acid reacts rapidly, no detectable disappearance of the chloroamine occurred in 7 hours. In acid solution, the rate of hydrolysis becomes measurable. It is unaffected by the amount of phenol present, is proportional to the acid strength, and is practically the same for nitric, sulphuric, and perchloric acids of the same concentration. If the rate of hydrolysis is the same in hydrochloric acid as in other acids, it is approximately 6% of the rate of chlorine formation in 0·1*M*-hydrochloric acid and decreases to 0·4% in 1·5*M*-acid. The rates of chlorine formation corrected for the rate of hydrolysis of the chloroamine give the speeds of direct interaction of the chloroamine and hydrochloric acid.

Activity of the Hydrochloric Acid.—Since the general activity reaction-velocity equation has been developed from the free-energy condition for equilibrium, $F_A + F_B = F_P + F_Q$, which applies strictly only to those equilibria in which a slight displacement does not affect the ionic strength, it is necessary to examine the reaction $(HCl \rightleftharpoons H^{\cdot} + Cl') + {:}NCl \longrightarrow Cl_2 + {:}NH$, more closely. Although the chlorine does not remain in the system, but is immediately taken up by other substances which are present, the velocity equation must satisfy the equilibrium conditions which would be attained were the chlorine to remain free in the system. For a

slight displacement of the above equilibrium such that dn mols. of hydrogen chloride disappear, there is a disappearance of $2dn$ ions, with a consequent decrease in the free electrical energy of the medium (Soper, *loc. cit.*). This change in the free energy of the medium is independent of whether the un-ionised acid or the ions actually react with the chloroamine. The equilibrium condition is therefore

$$-dF_{H^\cdot} - dF_{Cl'} - dF_{:NCl} + dF_{Cl_2} + dF_{:NH} - dF_{\text{medium}} = 0. \quad (2)$$

The interaction of hydrochloric acid and the chloroamine is apparently of the third order, but since it has the normal temperature coefficient (Harned and Seltz, *loc. cit.*), whilst a true termolecular reaction, involving the simultaneous collision of 3 molecules, has a temperature coefficient of nearly unity (Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68), it is probable that the reaction is one involving the un-ionised hydrogen chloride and the chloroamine. The partial free energy of the un-ionised hydrogen chloride is connected with those of the hydrogen and chlorine ions by the equation

$$-dF_{HCl} + dF_{H^\cdot} + dF_{Cl'} + dF_{\text{medium}} = 0 \quad . \quad . \quad (3)$$

where the dF_{medium} corresponds to the increase in the electrical free energy of the medium due to the formation of $2dn$ ions.

Combining (2) and (3), we have

$$-dF_{HCl} - dF_{:NCl} + dF_{Cl_2} + dF_{:NH} = 0,$$

or

$$F_{HCl} + F_{:NCl} = F_{Cl_2} + F_{:NH} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and substitution for $F_{HCl} = RT \log a_{HCl} + C_{HCl}$ etc., gives

$$a_{HCl}a_{:NCl}/a_{Cl_2}a_{:NH} = \text{constant},$$

corresponding to the simple activity reaction-velocity equation

$$v^* = -dc_{:NCl}/dt = k_0 a_{HCl} a_{:NCl} = k_0 a_{HCl} f_{:NCl} c_{:NCl}. \quad . \quad . \quad . \quad (5)$$

Values of a_{HCl} are given by *E.M.F.* measurements on hydrochloric acid concentration cells without liquid junction, for in a slight displacement of the system in equilibrium the electrical work $dnEF/N$ is balanced by the change in the partial free energy of

* The speed is regarded as the number of g.-mols. of the reagents reacting in unit time *per unit volume*, rather than the number reacting per unit weight of solution, for the activity is connected, as was pointed out by Scatchard (*loc. cit.*), with the number of molecules possessing a certain critical energy which enables them to pass through, or react with, unit area of the boundary surface in unit time. If one imagines a number of planes of unit area immersed in the solution, then those molecules possessing sufficient energy to carry them through the surface will also pass through each of these planes. If the planes are of infinitesimal thickness and are arranged so as to form a solid cube, the activity will measure the number of molecules possessing a certain critical energy in that cube, *i.e.*, in unit volume. The number of molecules reacting should also, therefore, have reference to unit volume.

the hydrochloric acid caused by its transference from cell to cell together with the net change in the electrical energy of the two media, *i.e.*,

$$dnE\mathrm{F}/N = -dF_{\mathrm{H'I}} - dF_{\mathrm{Cl'I}} - dF_{\mathrm{mediumI}} + dF_{\mathrm{H'II}} + dF_{\mathrm{Cl'II}} + dF_{\mathrm{mediumII}}$$

which, on being combined with (3), gives

$$dnE\mathrm{F}/N = -dF_{\mathrm{HClI}} + dF_{\mathrm{HClII}}$$

and $E\mathrm{F} = RT \log (a_{\mathrm{HClII}}/a_{\mathrm{HClI}}) + \text{constant}$.

Comparison of (5) with the equation $v = kc_{\mathrm{:NCl}}$ used in evaluating a velocity coefficient at any one acid concentration indicates that $k/a_{\mathrm{HCl}}f_{\mathrm{:NCl}}$ should be constant at constant temperature, unless the speed is affected by viscosity.

Effect of Viscosity.—Since activities, and therefore activity equilibrium constants, are independent of viscosity, it is possible to show theoretically by consideration of the equilibrium, $\mathrm{A} \rightleftharpoons \mathrm{P} + \mathrm{Q}$, that if the velocity of a unimolecular reaction is unaffected by viscosity, then that of a bimolecular reaction should also be unaffected; for application of the reaction-velocity equation to such an equilibrium gives $K = k_1/k_2$, and if K and k_1 are independent of viscosity, then k_2 must also be independent of it. This argument applies to any reaction-velocity equation of type (1).

In Table I the relative viscosities of the acid media (Green, J., 1908, **93**, 2023) have been included. The molalities (g.-mols. of acid per 1000 g. of water) are given in the first column, k' is the rate of chlorine formation, k'' the rate of hydrolysis of the chloroamine, $k = k' - k''$ is the rate of interaction of the chloroamine and hydrochloric acid, and a_{HCl} the activity measured electrometrically by Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 641).

TABLE I.

C_{HCl}.	$10^3 . k'$.	$10^4 . k''$.	$10^3 . k$.	$a_{\mathrm{H}} . a_{\mathrm{Cl}'}$.	$f_{\mathrm{:NCl}}$.	$\frac{k}{a_{\mathrm{HCl}}f_{\mathrm{:NCl}}}$	η.
0·1	0·52	0·32	0·49	0·00642	0·989	0·0767	1·000
0·2	1·88	0·58	1·82	0·02397	0·980	0·0775	1·005
0·3	4·06	0·96	3·95	0·05239	0·972	0·0775	1·011
0·4	7·11	1·25	6·98	0·09242	0·964	0·0783	1·017
0·5	10·8	1·50	10·6	0·1448	0·957	0·0772	1·023
0·6	16·0	1·92	15·8	0·2134	0·951	0·0778	1·029
0·7	21·9	2·24	21·7	0·2966	0·947	0·0779	1·035
0·8	29·1	2·54	28·9	0·3985	0·939	0·0773	1·042
0·9	38·2	2·88	37·9	0·5204	0·932	0·0779	1·043
1·0	48·2	3·24	47·9	0·6675	0·925	0·0776	1·054
1·5	124	4·80	124	1·843	0·877	0·0767	1·083

The values of $k/a_{\mathrm{HCl}}f_{\mathrm{:NCl}}$ are constant to within 1%, which is of the order of the experimental error, whilst the viscosity changes by 8%. The observed rates of reaction may therefore be regarded as supporting the simple activity velocity equation for a reaction

between neutral molecules in aqueous media. They do not necessarily indicate that the reactivity of an ion is proportional to its thermodynamic activity.

On Brönsted's theory (*Z. physikal. Chem.*, 1922, **102**, 169),

$$v = kc_{:NCl}\, c_{HCl} f_{:NCl} f_{HCl} / f_{(:NCl,HCl)}$$
$$= kc_{:NCl}\, a_{HCl} f_{:NCl} / f_{(:NCl,HCl)},$$

and comparison with the simple activity equation shows that, in order to account for the observed facts, the activity coefficient of the critical complex (:NCl, HCl) must be constant to within 0·5% over the acid range examined (0·1—1·5*M*). This is unlikely in view of the solubility changes which apparently almost invariably occur on addition of electrolytes to a solution.

Experimental.

Measurement of the Solubility of N-*Chloroacetanilide in Acid and Salt Solutions.*—Excess of *N*-chloroacetanilide was added to the salt solution and shaken for 15 minutes at 25·0°; 10 c.c. of the clear solution were then removed by a pipette attached to a glass tube, on the lower end of which was mounted a perforated platinum plate covered with filter-paper. The chloroamine present was estimated by running it into acidified potassium iodide solution and titrating the liberated iodine with *N*/100-thiosulphate. The mean of four titrations was taken after saturation was attained (approx. 15 mins.). The measured solubilities of *N*-chloroacetanilide (in g.-mols. per litre) in potassium chloride, potassium nitrate, and nitric acid solutions are given in Table II, together with the calculated solubility in hydrochloric acid.

Table II.

Ionic strength.	0·0.	0·1.	0·4.	0·7.	1·0.	1·5.
Solubility in KCl ...		0·01323	0·01232	0·01105	0·00963	0·00880
,, KNO_3.	(0·01383)	0·01350	0·01325	0·01275	0·01243	0·01178
,, HNO_3.		0·01418	0·01511	0·01680	0·01935	0·02295
,, HCl ...		0·01398	0·01434	0·01461	0·01495	0·01577

Speed of Chlorine Formation from N-*Chloroacetanilide and Hydrochloric Acid.*—The effect of increasing the concentration of acetanilide, phenol, or *p*-cresol on the rate of fall of the iodine titre of a mixture of *N*-chloroacetanilide and hydrochloric acid is shown in Table III :

Table III.

HCl = 0·2*M* :NCl = 0·01*M* ; temp. = 25·0°.

Concentration of phenol, *p*-cresol, or acetanilide, *M*	0·01.	0·02.	0·03.
100*k'* (acetanilide)	0·183	0·188	0·188
100*k'* (phenol)	0·186	0·188	0·188
100*k'* (*p*-cresol)	—	0·188	0·188

The limiting value for k which corresponds to the rate of chlorine formation from 0·01 M-chloroamine and 0·2M-hydrochloric acid is thus 0·00188. The limiting values for other acid concentrations are given in Table I. Care was taken when mixing the aqueous solution of chloroamine with the calculated weight of hydrochloric acid solution to adjust the initial temperatures so as to compensate for the heat of mixing. The speed of the reaction in the presence of 1·5M-hydrochloric acid is too great to allow of pipetting out portions of the mixture, and portions were therefore poured into weighed flasks containing potassium iodide and sodium acetate at 10-sec. intervals, the flasks were reweighed, and the contents titrated.

Speed of Hydrolysis of N-*Chloroacetanilide.*—Determinations of the rate of hydrolysis of the chloroamine were carried out in aqueous sulphuric, nitric, and perchloric acids, *p*-cresol being present in solution to remove the hypochlorous acid as formed. In the absence of acid, there is no detectable disappearance of the chloroamine in 7 hours. The rate of disappearance of chloroamine in the presence of acid follows a unimolecular velocity equation and the results obtained are summarised in Table IV.

TABLE IV.

:NCl = 0·01M; *p*-cresol = 0·1M; temp. = 25·0°.

Concentration of acid.	H_2SO_4.					HNO_3.	$HClO_4$.
	0·1	0·2	0·4	0·8	1·0	1·0	1·0
$k'' \times 10^4$	0·321	0·584	1·25	2·54	3·24	3·24	3·70

Summary.

1. Since concentration equilibrium constants are affected by the presence of electrolytes, the classical velocity coefficients are not true constants, and the use of an equation, $v = kf_{\text{catalyst}}C_AC_B$, for determining the effective concentration of the catalyst is not justifiable. Attention has therefore been redirected to the general form of a reaction-velocity equation.

2. The simplest type of the generalised equation applying to reactions involving neutral molecules, *viz.*, $v = ka_Aa_B$, is found to be in agreement with observations on the rate of interaction of hydrochloric acid and N-chloroacetanilide. The activities of the reagents used in the velocity equation are those which obtain in the presence of each other. Actually, the activity of the chloroamine was found to be progressively decreased by 13% as the hydrochloric acid concentration was increased from 0·1 to 1·5M.

3. The measurement of reaction speed in mols. transformed in unit time *per unit volume*, rather than per unit weight of solution, is justified on theoretical grounds.

4. A proof is advanced that reaction velocity is independent of viscosity.

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UNIVERSITY COLLEGE OF NORTH WALES,
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CCCLXIX.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part II. The Nitration of 1-Benzylpiperidine and of Some Related Substances.*

By ALFRED POLLARD and ROBERT ROBINSON.

ALTHOUGH it is now generally agreed that the *m*-directive effect of the ammonium-salt group in the benzylammonium salts is associated with the positive charge of the ion, there are still many aspects of the subject that call for elucidation. The majority of the constitutive influences that have been observed in this field are susceptible of simple explanations, for example, the somewhat higher *m*-direction in $CH_2Ph{\cdot}NMe_2$ than in $CH_2Ph{\cdot}NEt_2$ (Goss, Ingold, and Wilson, J., 1926, 2440) is the result to be anticipated from the theory of Allan, Oxford, Robinson, and Smith (J., 1926, 401), the terminal methyl groups in the latter compound having a smaller electron affinity than the hydrogen atoms which they may be regarded as displacing. Thus in the benzyldiethylammonium ion the positive charge of the nitrogen atom is neutralised by electron displacement towards it to a larger extent than is the charge of the nitrogen atom in the benzyldimethylammonium ion. Considerations like these, although frequently applicable, cannot be extended, however, to benzylpiperidine, from which the yield of *m*-nitro-derivative is notably higher than that from the closely related tertiary bases already mentioned. Noelting and Kregczy (*Bull. Soc. chim.*, 1916, **19**, 355) found that benzyldiethylamine on nitration in sulphuric acid solution gave from 35—40% of the *m*-nitro-derivative; Flürscheim and Holmes (J., 1926, 1562) found 33—53% under various conditions in sulphuric acid solution. Goss, Ingold, and Wilson (*loc. cit.*), employing nitric acid (*d* 1·5) alone, found that the proportion of the *m*-isomeride formed was 51%, and we have confirmed this. On the other hand, we were aware that the estimate of the proportion of the *m*-nitro-isomeride formed in

the nitration of benzylpiperidine, that was based by Ing and Robinson (J., 1926, 1665) on the separation as hydriodide, namely 60%, was a conservative one. Employing Francis and Hill's bromination method (*J. Amer. Chem. Soc.*, 1924, **46**, 2498), we find that 72% of *m*-nitrobenzylpiperidine is actually formed. Similarly, 1-β-*phenylethylpiperidine*, $C_5H_{10}N{\cdot}CH_2{\cdot}CH_2Ph$, obtained by the interaction of magnesium benzyl chloride and *N-iso*butoxymethylpiperidine in accordance with the general method of Robinson and Robinson (J., 1923, **123**, 532), gave on nitration about 22% of its *m*-nitro-derivative. This figure is higher than that found for the simpler dialkylated β-phenylethylamines (compare Goss, Hanhart, and Ingold, J., 1926, 250) and confirms the benzylpiperidine case. We are aware that this pronounced effect of ring closure may be accounted for merely as the result of a composition difference of two hydrogen atoms, our knowledge being insufficient to enable us to exclude this possibility on *a priori* grounds; we are nevertheless of the opinion that such a simple view is inadequate and, in the sequel, propose an alternative.

Flürscheim and Holmes (*loc. cit.*) showed that the proportion of *m*-nitrobenzyldiethylamine formed in the nitration of the salt of the base in sulphuric acid was diminished by saturation of the solution with ammonium sulphate. We have extended the study of this phenomenon to the nitration of benzylpiperidine in nitric acid solution. The addition of ammonium nitrate reduced the proportion of *m*-isomeride formed to about 56%, but as this salt is not readily soluble in nitric acid we made a further series of experiments on the influence of the addition of trimethylammonium nitrate to the acid, and found that the proportion of *m*-isomeride formed could be reduced to 16%. Addition of rubidium nitrate, which is readily soluble in nitric acid, produced roughly the anticipated effect. Addition of urea also decreased the proportion of the *m*-isomeride formed, and this was due to Flürscheim's effect and not to the removal of nitrous acid, because when nitric acid freed from nitrous acid by means of lead peroxide or by hydrogen peroxide was employed for the nitration of benzylpiperidine the normal proportion of the *m*-isomeride was formed.

These variations in orientation produced by the addition of salts are unexpectedly great and demonstrate that the condition of the kation is of primary importance in determining the nature of the observed results. We attribute the effect to the progressive electrostriction of the kations by the nitrate ions, an explanation which is the equivalent, in the modern theory, of Flürscheim and Holmes's suggestion that the ion undergoes substitution in the *m*-position and the undissociated salt in the *o*- and *p*-positions. On any theory, the

results make it evident that the value obtained in an experiment in which the base is gradually added to the nitric acid represents a mere average, since the ionic concentration is progressively increased during the nitration. This must coincide with a decreasing rate of formation of the *m*-isomeride relative to that of the *p*-isomeride. (Attempts to define and apply standard conditions are being made.) Nevertheless we have found that the results obtained in the nitrations are reproducible and, although the numbers representing the proportions of *m*-isomeride formed have not the character of fundamental constants, some conclusions may be drawn from a consideration of these averages obtained in the case of related bases. It would, for example, appear most probable that the proportion of *m*-isomeride formed is partly related to the existence of constitutive factors that either hinder or assist the operation of electrostriction of the kations. In this connexion stereochemical conceptions are of primary importance (compare Flürscheim's steric factor, *s*, in the correlation of the strengths of bases with their constitutions), because it is clear that the anions or negative ends of polarised complexes can the more effectively modify the field of the positively charged nitrogen atom the closer they can approach it. Other things being equal, we should expect the degree of electrostriction of the kations to be influenced as follows:

(1) *The smaller the number of atoms directly attached to the central charged atom, the greater should be the degree of electrostriction.* The present authors have studied the nitration of a benzyldiethylsulphonium salt and will shortly submit an account of the work. The proportion of *m*-isomeride formed, although still noteworthy, is very much lower than in the nitration of benzyltrimethylammonium nitrate. We attribute the result partly to the fact that the central atom is surrounded by four atoms in the ammonium salt, but by only three in the sulphonium salt. Benzylmethylpiperidinium nitrate, $CH_2Ph{\cdot}NMe{:}[CH_2]_5{}NO_3$, gave more than 90% of the *m*-nitro-derivative on nitration, and the proportion of the *m*-nitro-isomeride formed in the nitration of benzylpyridinium perchlorate was estimated to be about 67%. The nitrogen atom is attached to four atoms in the first case, but to only three in the second. This explanation of the result is adequate, but we do not exclude the possibility that the charge may be distributed over the pyridine nucleus to some extent by induction and may thus be less effective on account of electron displacements towards it.

(2) *The greater the volume of the central charged atom the greater should be the degree of electrostriction.* In this case, the larger radius might be expected to hinder electrostriction, but this effect may be

ignored, since it also places the charge further away from the aromatic nucleus, and this in itself diminishes the intensity of the field. On the other hand, electrostriction should be facilitated in the larger atoms by the smaller electron density near the surface rendering such atoms *softer* and perhaps by the appearance of patches not covered by the surrounding atoms. Thus under comparable conditions we may anticipate diminishing *m*-substitution in ascending a group in the periodic system: *e.g.*, $CH_2Ph{\cdot}NR_3 > CH_2Ph{\cdot}PR_3 > CH_2Ph{\cdot}AsR_3 > CH_2Ph{\cdot}BiR_3$, and $CH_2Ph{\cdot}SR_2 > CH_2Ph{\cdot}SeR_2$.

(3) *The smaller the space occupied by the atoms or groups attached to the central charged atom, the greater should be the degree of electrostriction.* This consideration clearly applies to the case of hydrogen atoms, which have even been regarded as embedded in the electron shells (Thomson, Paneth). The nakedness of the proton is necessarily a most important factor favouring electrostriction in the salts of primary, secondary, and tertiary bases in diminishing degree. In other examples, the electron displacements and distances separating the atomic centres must also be taken into account.

(4) *The greater the mobility of the groups surrounding the central charged atom, the greater should be the degree of electrostriction.* We imagine that closer approach of the anions is possible when the surrounding groups can be pushed aside or when, as the result of their normal vibrations, there are phases in which the nucleus of the central atom is exposed. Herein, we suggest, lies the explanation of the benzylpiperidine case. In benzyldiethylamine, the ethyl groups are not fixed, but may be supposed to be capable of some movement over a limited area of the surface of a sphere. When the ends of the chains are joined together as in benzylpiperidine, this freedom of movement must be lessened and electrostriction would be hindered in consequence. It is proposed to test this hypothesis by instituting further comparisons between open-chain and cyclic bases. The highest proportion of the *m*-derivative should be formed in the nitration of *N*-alpharylquinuclidinium salts, since the molecular framework in this series should be especially rigid.

The course of the nitration of benzylpiperidine was unaffected by the addition of nitromethane or ethyl malonate to the reaction mixture, and the addition of nitrobenzene only lowered the proportion of *m*-isomeride formed to 58%. Evidently these weak bases do not form true ionised salts with nitric acid, and we suggest the following conception of the nature of the solutions. It is generally recognised that, in an acid HX, X has a more or less pronounced affinity for the negative charge and by electron displacement the nucleus of the proton is bared so that HX is polarised. In a base

Be (e = electron) of the type that might form a salt BeH}X, B has a more or less pronounced affinity for the positive charge, and this molecule also is polarised (or there may be a tendency to polarisation consummated by induction). In an acid, therefore, there are an intense local positive field and a diffuse negative field; in a base, the negative field is the more concentrated. The respective complexes thus contain *bound* ions (although the charges are not integral), and the ever-changing interplay of the forces between these is the interpretation we offer of the expression " loose additive complex " which might be applied to the cases considered. This hypothesis gives a very similar picture of the condition of salts and of additive complexes in solution. In both cases, moderately stable molecules containing a limited number of the components may exist for definite periods of time.

EXPERIMENTAL.

Method of Estimation of the Proportion of m-*Isomeride formed.*—In applying the method of Francis and Hill (*loc. cit.*) to the products of nitration of benzylpiperidine, we found that the presence of small quantities of unchanged benzylpiperidine did not affect the results and that the best procedure was to analyse directly the mixture of bases obtained. An important precaution was the avoidance of too large an excess of titanous chloride or of bromine. The nitro-compounds present were first estimated by reduction with titanous chloride and back-titration with ferric alum; reduction with a slight excess of titanous chloride was then effected in a fresh experiment, followed by bromination at 0° with the usual precautions. Within the limits of experimental error, the pure *o*-, *m*-, and *p*-nitrobenzyl-piperidines (Lellmann and Pekrun, *Annalen*, 1890, **259**, 40) (purity estimated by means of titanous chloride, 99—100%) required after reduction 2, 3, and 2 molecular proportions of bromine, respectively. The fact that stoicheiometric rather than empirical relations can be employed in the calculations was confirmed by the analysis of the following mixtures: *ortho*, 48·4% and *meta*, 51·6% (Found: *meta*, 48, 51·4%); *meta*, 48% and *para*, 52% (Found: *meta*, 44, 47, 52%); *meta*, 71% and *para*, 29% (Found: *meta*, 69, 72%).

Nitration of Benzylpiperidine.—The nitration (of 5 g.) was carried out as described by Ing and Robinson (J., 1926, 1664) and the bases were isolated by means of ether. The mononitration was almost theoretical (Found: *meta*, 66, 71, 72, 76, 77; mean, 72%). In subsequent experiments, the conditions of nitration were the same (3 g. of the base and 20 c.c. of nitric acid, d 1·50) and the yields were from 90—98%. When relatively large amounts of ammonium nitrate were added, stirring was rendered difficult by the separation

of solids from the solution when it was cooled to −15°. These may contain $NH_4NO_3,2HNO_3$, but also, in all probability, a similar complex derived from benzylpiperidinium nitrate, because the proportion of the base that was nitrated under the standard conditions was very much lower than in other cases. The results were: addition of ammonium nitrate (5 g.) (Found: nitration, 95%; *meta*, 57, 59, 59%); addition of ammonium nitrate (7 g.) (Found: nitration, 17·8%; *meta*, 54, 58%); addition of ammonium nitrate (8 g.) (Found: nitration, 24·5%; *meta*, 54, 56%).

Lithium, sodium, potassium, and rubidium nitrates form a series in which the solubility in nitric acid increases, lithium nitrate being very sparingly soluble and rubidium nitrate being freely soluble. Addition of rubidium nitrate (3 g.) gave a clear reaction mixture (Found: nitration, 98%; *meta*, 19, 23·4, 25%). From the results tabulated below, it was found that the equivalent amount of trimethylammonium nitrate should reduce the proportion of the *m*-isomeride formed to 24%.

Trimethylammonium nitrate was crystallised from alcohol until its m. p. was 152—153°. The effects of additions of this salt are shown in the following table:

$NHMe_3NO_3$ added (g.).	Nitration (%).	*Meta* (%).	Mean.
0·5	98·3	59, 62, 66, 71	64
1·0	99·3	50, 53	51·5
1·5	96·0	40, 40, 41	40
2·0	98·7	30, 31, 33	31·3
3·5	81·3	15, 16, 17	16
7·0	90·9	21, 21	21

The result with 7·0 g., indicating a rise in *m*-isomeride formation after a minimum value has been reached, will be further investigated when the conditions are more accurately defined. The percentage nitration of the base in this case was confirmed by reducing the product (1·62 g.) with zinc and dilute sulphuric acid, the resulting amines being then benzoylated and the unchanged benzylpiperidine isolated by distillation in steam. The picrate (0·18 g.) was obtained in canary-yellow crystals, m. p. 174—176°; mixed with the picrate of benzylpiperidine, m. p. 175—177°, it melted at 174°. We were thus able to isolate as picrate 67% of the unchanged benzylpiperidine which the titanous chloride estimation indicated to have been present in the nitration product.

Since the rate of predominating *m*-substitution in a monosubstituted benzene derivative is always lower than that of predominating *op*-substitution (Holleman), it seemed possible that the degradation of the reagent might result in a diminution of the proportion of the *m*-isomeride formed. The gradient of the curve representing the relation between reaction velocity and chemical

activity of the reagent should, in other words, be steeper in the case of the formation of the *m*-isomeride. This consideration might have a bearing on the effect of addition of salts to the nitric acid, and we therefore tried another method of degradation, namely, the removal of nitrous acid. Urea (1·0 g.) was added to nitric acid (20 c.c.; *d* ·51), which was then cooled in a freezing mixture and thereafter allowed to warm to the ordinary temperature (the density became 1·52); after cooling again, the mixture was employed in a nitration under the standard conditions (Found: nitration, 99%; *meta*, 45, 45%). Lead peroxide was added to nitric acid (*d* 1·53), mixed with a little acid (*d* 1·54) prepared by distillation of a mixture of nitric acid (*d* 1·51) and phosphoric anhydride; after filtration the acid had *d* 1·51 and was free from lead. The nitration was carried out with this specimen in the presence of a small amount of lead peroxide (Found: nitration, 94%; *meta*, 65, 69, 73%). Another specimen of nitric acid (*d* 1·5) was prepared by the addition of concentrated aqueous hydrogen peroxide to nitric acid (*d* 1·54), and this was employed in the nitration (Found: nitration, 98%; *meta*, 71%).

When the standard nitration conditions were modified by reduction of the volume of nitric acid to 10 c.c., a small diminution in the proportion of *m*-isomeride formed was observed (Found: nitration, 95%; *meta*, 61, 62, 64%), but when the volume of nitric acid employed for the nitration of 3 g. of the base was trebled (60 c.c.) some dinitration occurred.

The following results were obtained under the standard conditions modified as stated: Addition of nitrobenzene (5 g.) (Found: nitration, 98%; *meta*, 57, 59%); addition of nitromethane (2·5 g.) (Found: nitration, 99%; *meta*, 70, 73, 73%); addition of ethyl malonate (6·5 g.) (Found: nitration, 97%; *meta*, 69, 69%).

Benzyldiethylamine was nitrated under the conditions used for benzylpiperidine (Found: nitration, 98%; *meta*, 48, 50, 51%).

Nitration of Benzylmethylpiperidinium Nitrate.—Benzylmethylpiperidinium iodide, prepared from benzylpiperidine and methyl iodide, crystallises from ethyl alcohol in colourless needles, m. p. 147° (Found: I, 40·0. $C_{13}H_{20}NI$ requires I, 40·1%). It is readily soluble in water and in hot alcohol.

This salt was converted into the *nitrate* by exact decomposition with silver nitrate, and the aqueous solution was evaporated to a syrup and then in a vacuum over sulphuric acid for several months. The friable solid was extremely hygroscopic, liquefying in the air in a few seconds; an estimation by means of nitron, combined with a titration showing the amount of free nitric acid present, indicated that the material contained 99—100% of the quaternary nitrate.

The salt (20 g.) was added to nitric acid (80 c.c.; *d* 1·5) at 0° during 15 minutes, and the solution kept at this temperature for 2 hours and at room temperature for 2 hours more. The liquid was then diluted and distilled under diminished pressure, and this process was repeated so as to remove most of the nitric acid. The residue was neutralised with ammonia, and the picrate precipitated by stirring for 1 hour with an excess of picric acid. The mixture of picrate and picric acid was collected, washed with aqueous picric acid, and mechanically shaken with ether and dilute hydrochloric acid until no solid remained. The acid aqueous solution was concentrated under diminished pressure, again extracted with ether, and then neutralised with ammonia and concentrated to about 100 c.c. The iodide was then precipitated by the addition of a large excess of sodium iodide (yield, 94%). The crude nitration product (10 g.) was fractionally crystallised from methyl alcohol; 9·7 g. of the pure *m*-isomeride were obtained (Found: I, 35·0%), and the colour reactions of the last mother-liquor showed that it still contained the *m*-isomeride in preponderating amount, a little of the *p*-isomeride, and a yellow impurity.

The three nitrobenzylmethylpiperidinium iodides were prepared from the nitrobenzylpiperidines and methyl iodide and dried at 100° for analysis. o-*Nitrobenzylmethylpiperidinium iodide* crystallises from methyl alcohol in intensely yellow prisms, m. p. 183—184° (Found: I, 34·9. $C_{13}H_{19}O_2N_2I$ requires I, 35·1%). This salt develops a brownish-yellow colour in boiling methyl-alcoholic potassium hydroxide, and on the addition of a methyl-alcoholic solution to acetone and solid potassium hydroxide a bright brownish-red solution is obtained.

m-*Nitrobenzylmethylpiperidinium iodide* crystallises from methyl or ethyl alcohol in very pale yellow needles which darken at 198° and melt at 204° (Found: I, 35·1%). It gives no coloration in boiling methyl-alcoholic potassium hydroxide, but when a methyl-alcoholic solution is added to acetone and solid potassium hydroxide an intense and characteristic violet colour is developed.

p-*Nitrobenzylmethylpiperidinium iodide* crystallises from water or methyl alcohol in large, well-developed, yellow prisms, and from ethyl alcohol in pale yellow needles, m. p. 188° (decomp.) (Found: I, 34·9%). This salt develops a reddish-brown coloration in boiling methyl-alcoholic potassium hydroxide, and a dull mauve-red one when a methyl-alcoholic solution is added to acetone and solid potassium hydroxide.

These salts exhibit colour reactions under other conditions, but those recorded above were selected, after numerous trials, for the purpose of assisting in the identification of specimens. It will be

observed that under one set of conditions the *m*-isomeride gives no reaction whereas the *o*- and *p*-isomerides develop colorations; under the other set of conditions the *m*-isomeride gives the most characteristic reaction.

Nitration of Benzylpyridinium Perchlorate.—Aqueous perchloric acid was added to a solution of benzylpyridinium chloride; the precipitated oil crystallised in contact with ice-water. The dry salt (20 g.) was added during 45 minutes to nitric acid (100 c.c.; *d* 1·5) at 0°; the mixture was kept at this temperature for 1 hour and then allowed to warm to the temperature of the room during 1·5 hours. The solution was diluted, the greater part of the nitric acid distilled under diminished pressure, an excess of perchloric acid (*d* 1·12) added, and the mixture kept in the ice-chest for 24 hours; the precipitated perchlorates were then collected, washed, and dried (A) (20·5 g.) (Found: C, 45·8; H, 3·6. $C_{12}H_{11}O_6N_2Cl$ requires C, 45·9; H, 3·5%). In another experiment, the nitric acid was not removed and the crystallisation of the perchlorates was carried out fractionally, crops of approximately 12 g., 5 g., and 3 g. being obtained. On recrystallisation, the first fraction gave pure *m*-nitrobenzylpyridinium perchlorate, but the separation could not be carried out in a quantitative manner. Oxidation of the crude nitration product with potassium permanganate gave *m*- and *p*-nitrobenzoic acids, which were separated and identified; the yields, however, were not satisfactory. It was found possible to apply Francis and Hill's bromination method to this case, because the nitrobenzylpyridinium perchlorates may be quantitatively reduced to aminobenzylpyridinium chlorides by means of titanous chloride. This is not effected, however, under the ordinary conditions and the following experiment indicates the modifications required. A solution of *p*-nitrobenzylpyridinium perchlorate (0·1000 g.) in 50% sulphuric acid (25 c.c.) and water (150 c.c.) was boiled with titanous chloride for 20 minutes with the usual precautions, care being taken to avoid undue concentration (Found: titanous chloride solution used, 37·2 c.c. Calc. for complete reduction, 37·3 c.c.). Applying this method of reduction to the product (A), followed by bromination in the usual manner, we found *meta*, 64, 69, 69%. A mixture of *m*-nitrobenzylpyridinium perchlorate (70%) and *p*-nitrobenzylpyridinium perchlorate (30%) was similarly analysed (Found: *meta*, 69, 71%).

The isomeric nitrobenzylpyridinium perchlorates were prepared by addition of perchloric acid to solutions of the corresponding chlorides or bromides.

o-Nitrobenzylpyridinium perchlorate crystallises from alcohol in colourless, elongated, rhombic prisms, m. p. 155—156° (Found: C,

46·1; H, 3·5. $C_{12}H_{11}O_6N_2Cl$ requires C, 45·9; H, 3·5%). The action of boiling aqueous sodium hydroxide on this salt causes a decomposition, one of the products of which is *o*-nitrotoluene.

m-*Nitrobenzylpyridinium perchlorate* crystallises from alcohol in colourless, prismatic needles, m. p. 176—177° (Found: C, 46·0; H, 3·6%).

p-*Nitrobenzylpyridinium perchlorate* crystallises from alcohol in colourless, elongated laminæ, m. p. 181—182° (Found: C, 46·0; H, 3·6%). The long, flat plates have jagged edges and well-formed pointed or square-cut ends and exhibit a strong twinning tendency. On boiling with sodium hydroxide solution, *p*-nitrotoluene is produced.

1-β-*Phenylethylpiperidine.*—The preparation of 1-*iso*butoxymethylpiperidine (McLeod and G. M. Robinson, J., 1921, **119**, 1474) is conveniently carried out on a moderately large scale. A mixture of piperidine (400 g.) and *iso*butyl alcohol (400 g.) was added to 40% aqueous formaldehyde solution (400 g.) with cooling in running water; the mixture was saturated with potassium carbonate and kept over-night and the oil was then dried with fresh potassium carbonate. On distillation, 665 g., b. p. 200—210°, were obtained (yield, 83%). The considerations dictating the use of *iso*butyl alcohol are that the higher alcohols give the better yields, and that some decomposition occurs in the distillation of 1-*n*-butoxymethylpiperidine under ordinary pressure. *iso*Butoxymethylpiperidine (120 g.) was slowly added to an ethereal solution of magnesium benzyl chloride (from 100 g. of benzyl chloride, 20 g. of magnesium, and about 1500 c.c. of ether), a violent reaction ensuing after each addition. Water was then cautiously introduced with shaking until a clear ethereal layer could be decanted from the magnesia sludge; the latter was washed with fresh ether. The base was extracted from the ethereal solution by successive small volumes of dilute hydrochloric acid, and any unchanged *iso*butoxymethylpiperidine decomposed by heating the acid solutions for 15 minutes on the steam-bath. The base was then set free by means of sodium hydroxide, separated, dried with sodium hydroxide, and distilled. 105 G., b. p. 162°/35 mm., of a colourless oil were obtained (yield, 80% calculated on the *iso*butoxymethylpiperidine) (Found: equiv., 189·3. Calc., 189·2). The b. p. /760 mm. was 262—264° with some decomposition. The *picrate* crystallised from alcohol in perfectly straight, canary-yellow needles, m. p. 144—145° (Found: N, 13·4. $C_{19}H_{22}O_6N_4$ requires N, 13·4%). The length of the individual crystals seems to be limited only by the shape of the container and the volume of the solution; those which we obtained were about 8—10 cm. long.

On nitrating the base under the conditions used for benzylpiperidine, and assuming the stoicheiometric relation for the bromination of the *m*- and *p*-amino-derivatives, we found: nitration, 98%; *meta*, 20, 22·7, 24%.

1-*γ*-*Phenylpropylpiperidine*, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}[CH_2]_5$.—The method described in the last section was applied, the initial materials being phenylethyl bromide (98 g.), magnesium (12·5 g.), and *iso*butoxymethylpiperidine (85 g.). 59 G. of a colourless oil, b. p. 150°/15 mm., were obtained (yield, 58%) (Found: equiv., 202. Calc., 203). This base has b. p. 272—274°/760 mm. with decomposition. The *picrate* crystallises from alcohol in bright yellow tablets, m. p. 99—100° with slight previous softening (Found: N, 13·0. $C_{20}H_{24}O_6N_4$ requires N, 13·0%).

In this case, nitration with nitric acid (*d* 1·5) causing some dinitration, the standard conditions were employed with nitric acid having *d* 1·465 (Found: nitration, 99%; *meta*, 5, 6, 8%).

We desire to thank the Department of Scientific and Industrial Research for grants which have enabled one of us to take part in the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, September 2nd,* 1972.]

CCCLXX.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part III. The Nitration of* m-*Nitrophenylbenzylsulphone.*

By BIBHUCHARAN CHATTERJEE and ROBERT ROBINSON.

THE hypothesis (Allan, Oxford, Robinson, and Smith, J., 1926, 401) that the positive charge of the dipole in the nitro-group of phenylnitromethane is the cause of the *m*-substitution observed by Holleman, and the related wider theory, can be tested experimentally in many directions, the most obvious of which is the study of the orienting influence in aromatic substitution of polar and dipolar groups situated at various distances from the nucleus. This field of systematic work is too large to be covered by any one group of investigators, but the exploitation of it by Ingold and his co-workers has involved some duplication of research, particularly in connexion with the nitration of phenylethylamine derivatives and of substances of the forms $Ph{\cdot}CO{\cdot}R$ and $Ph{\cdot}CH_2{\cdot}SO_2R$. Some preliminary experiments in the latter group are described in this and the following communication.

The interest of the toluene-ω-sulphonyl compounds resides in their theoretical analogy with the phenylnitromethanes, the double dipole $-\overset{++--}{SO_2}$ being compared with the single dipole $-\overset{+-}{NO_2}$, and in the fact that the effect of varying the group R can be observed. We selected the case of *m*-nitrophenylbenzylsulphone because we thought that the group $-C_6H_4\cdot NO_2(m\text{-})$ should be almost neutral and the results could therefore be ascribed to the influence of the sulphone group. The proportions of the *o*-, *m*-, and *p*-isomerides formed on nitration, estimated by colorimetric methods which are fully described in the experimental section, were approximately 25, 28, and 47%, respectively. The double semi-polar double bond of the sulphone group has thus a smaller *m*-orienting effect than the single semi-polar double bond of the nitro-group. This constitutes a definite argument against the view that the charges in the semi-polar double bonds are integral and effective as such.

As Born (compare *Ann. Reports*, 1926, 261) has shown, kations and anions are distorted and polarised in the neighbourhood of each other, and if this is true of the components of a molecule of sodium chloride, how much more must it be true of the bound ions in a semi-polar double bond. In fact, the intensity of the external fields may be chiefly governed by this atomic polarisation. On this basis, we may conclude that the kationic charge of the sulphur atom in the sulphone group is less effective than that of the nitrogen in the nitro-group and that this is due to the relatively greater degree of polarisation of the oxygen atoms in the sulphone; this again is clearly connected with the larger nuclear charge of the sulphur atom and the smaller electron density of its outer shell.

Ingold, Ingold, and Shaw (this vol., p. 813) found that the nitration of benzylmethylsulphone gave about 30% of the *m*-nitro-isomeride, but these authors attributed the result (comparison with phenylnitromethane) to absorption of the effect of the ionic charge of sulphur in passing through the outer shells of the atom. This suggestion appears to be fallacious owing to the circumstance that in the calculation of the kationic charges, for example, + 1, + 2, or + 6, in various theories respecting sulphur compounds, the electrons of the outer shells are taken into account or assumed to be donated to other atoms. Probably the distance separating the centres of sulphur and carbon atoms in C—S is greater than that separating the centres of carbon and nitrogen atoms in C—N and this must reduce the effectiveness of equivalent charges in accordance with Coulomb's Law; if the charges are not equivalent, the validity of this explanation is greatly impaired.

Our view that the bound oxygen ions are polarised, thus reducing

the net charge of the sulphur atom, is closely connected with the theory of electrostriction of sulphonium kations by free anions; it is, in fact, intramolecular electrostriction. It should be noted that this hypothesis emphasises the importance of the part played by the central atom and can be correlated experimentally with work on the distribution of electrons in crystals. The hypothesis is also connected with the strength of the sulphonic acids, for it is surely the polarisation of the oxygen atoms in the $R{\cdot}SO_3$ ion that loosens the grip of their electrons on the proton (alternatively, increases the repulsion of the proton by the oxygen nucleus).

EXPERIMENTAL.

m-*Nitrophenylbenzylsulphone*, $NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2Ph$.—A mixture of sodium *m*-nitrobenzenesulphinate (20 g.), benzyl chloride (15 g.), and 95% alcohol (60 c.c.) was refluxed for 4 hours, and the product (18 g.) precipitated by the addition of water. The *sulphone* crystallised from alcohol in very pale yellow needles, m. p. 151—152° (Found: C, 56·8; H, 4·5; N, 5·2. $C_{13}H_{11}O_4NS$ requires C, 56·3; H, 4·0; N, 5·1%).

m-*Nitrophenyl*-o-*nitrobenzylsulphone* was similarly prepared from *o*-nitrobenzyl chloride (8 g.), the yield being 14·7 g. It crystallised from acetone in pale yellow plates, m. p. 192—193° (Found: C, 48·6; H, 3·5; N, 9·0. $C_{13}H_{10}O_6N_2S$ requires C, 48·5; H, 3·1; N, 8·7%).

m-*Nitrophenyl*-m-*nitrobenzylsulphone* crystallised from alcohol in almost colourless, microscopic cubes, m. p. 194—195° (Found: C, 48·5; H, 3·0; N, 8·5%).

m-*Nitrophenyl*-p-*nitrobenzylsulphone* crystallised from acetone in very pale yellow needles, m. p. 180—181° (Found: C, 48·8; H, 3·6; N, 9·0%). The three isomerides are very sparingly soluble in most organic solvents and although the *o*-isomeride is the most sparingly soluble in alcohol, neither this nor any other solubility property could be employed for their separation.

Nitration of m-*Nitrophenylbenzylsulphone*.—The finely powdered substance (5·00 g.) was gradually added during 15 minutes to nitric acid (40 c.c.; *d* 1·5) kept at − 5° to 0°. Each addition produced a brownish-red, evanescent coloration. After 1 hour, the mixture was allowed to reach the room temperature and the product was precipitated by water after 3 hours. It was ground under water, washed, and dried (5·63 g. or 97%). In a second similar experiment the yield was 98·5% (Found: C, 48·6; H, 3·4%).

Various attempts to fractionally crystallise this material were made, but no suitable solvent could be found, and after experi-

menting with oxidation methods, which also we were compelled to abandon on account of the sparing solubility of the isomerides, we adopted the following colorimetric method. The *p*-isomeride gives a carmine coloration in alcoholic solution on the addition of 10% aqueous sodium hydroxide, whereas the *o*- and *m*-isomerides give no coloration under these conditions. In dilute solutions, the intensity of this colour was roughly proportional to the concentration of the *p*-isomeride and it was not affected by the presence of the *o*- or *m*-isomeride. A Zeiss "Stufenphotometer" was employed for the measurements and all the comparisons were direct, and not through a standard. The liquids were mixed in the adjustable vessels so that the colours could be compared as quickly as possible, and stirring was necessary before the caps were screwed on. Remarkably consistent results were obtained. Solutions of the nitration product (0·1987 g.), the *o*-isomeride (0·2018 g.), the *m*-isomeride (0·2098 g.), and the *p*-isomeride (0·2023 g.) in absolute alcohol (1000 c.c. each) were prepared. Taking 10 c.c. of the standard solution and adding 2 c.c. of 10% aqueous sodium hydroxide, it was found that the solution of the *p*-isomeride was roughly twice as concentrated (in *p*-isomeride) as the solution of the nitration product, columns of 5·35, 6·0, and 6·9 mm. balancing columns of 10·7, 11·9, and 13·8 mm., respectively. A closer comparison was then made by diluting the solution of the *p*-isomeride with an equal volume of alcohol and producing the colour as before; the solution of the *p*-isomeride was distinctly the stronger, the measurement indicating that the nitration product contained 47% of the *p*-isomeride. A mixture of the solution of the *p*-isomeride (45 c.c.) and alcohol (55 c.c.) gave a perceptibly weaker colour than the solution of the nitration product, the measurement again indicating that the nitration product contained 47% of the *p*-isomeride. The experiment was twice repeated with exactly the same results, so that the determination of the proportion of the *p*-isomeride in the mixture was considered to be sufficiently accurate to be employed in further work.

The estimation of the proportions of the *o*- and *m*-isomerides was much more difficult and the method was not capable of very great accuracy; the experiments were, however, frequently repeated and it is hoped that the results are not seriously in error. The *o*-isomeride gives an intense violet coloration with strong alkalis in alcoholic acetone (or pure acetone) solution, whereas the *m*-isomeride gives no immediate coloration. The following solutions were employed: (1) *o*-isomeride (5 c.c.), *p*-isomeride (20 c.c.), alcohol (17·5 c.c.); (2) *o*-isomeride (10 c.c.), *p*-isomeride (20 c.c.), alcohol (12·5 c.c.); (3) *o*-isomeride (15 c.c.), *p*-isomeride (20 c.c.), alcohol

(7·5 c.c.); (4) *o*-isomeride (20 c.c.), *p*-isomeride (20 c.c.), alcohol (2·5 c.c.); (5) nitration product (42·5 c.c.). Sodium ethoxide solution (10 c.c.) (from 10 g. of sodium in 250 c.c. of alcohol) and then pure acetone (50 c.c.) were added to each mixture. The colour developed by the nitration product was found to lie between those produced by solutions (2) and (3) and was much closer to that of (2). Experiments with solutions of compositions between those of (2) and (3) confirmed this and indicated that the nitration product contained 25—30% of the *o*-isomeride. The colour-tone match was not perfect, however, and it was then noticed that the *m*-isomeride slowly developed a brownish-red coloration in acetone solution in the presence of sodium ethoxide. A fresh series of solutions was therefore made up in which the pure alcohol was replaced by the appropriate volume of the *m*-isomeride solution; a colour-tone match was then obtained and the intensity showed that the proportion of the *o*-isomeride in the nitration product was 23—27%. This was confirmed by a direct estimation of the content of *m*-isomeride.

The three isomerides develop colorations when solid potassium hydroxide is added to their cold solutions in acetone, but if, after a short time, water is added, the colorations due to the *o*- and *p*-isomerides are discharged and the *m*-isomeride gives a brownish-yellow solution. A series of mixtures was prepared as before from the standard alcoholic solutions and, after the alcohol had been removed, acetone (30 c.c.) and potassium hydroxide (2 cm. stick) were added. The mixture was stirred for 5 minutes, water (50 c.c.) was then added, and the colour compared with that obtained from the nitration product under identical conditions. The proportion of the *m*-isomeride in the nitration product was thus found to lie between 25 and 32%. A mixture of the *o*-isomeride (0·250 g.), the *m*-isomeride (0·280 g.), and the *p*-isomeride (0·470 g.) was then made and its colour reactions were compared with those of the nitration product, the substances being weighed on a micro-balance, with the result that no difference could be detected. The mixture after fusion, resolidification, and grinding had m. p. 152—156° and the nitration product had m. p. 153—157°; a mixture of the two had m. p. 152—156°.

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CCCLXXI.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part IV. The Nitration of Toluene-ω-sulphonic Acid and of Toluene-ω-sulphonyl Chloride.*

By ARTHUR C. BOTTOMLEY and ROBERT ROBINSON.

THE work of Vorländer (*Ber.*, 1919, **52**, 262) proved that an atom bearing a positive charge when directly attached to the aromatic nucleus has a powerful *m*-directive effect, and on the lines of electronic theories this may be interpreted as meaning that a group having a strong attraction for electrons has a *m*-directive effect. The discovery of the largely predominating *meta*-nitration of benzyltrimethylammonium nitrate (Part I, J., 1926, 1655) justified this view in the most convincing manner. It may be fairly claimed that the connexion between polarity and orientation thus firmly established is less hypothetical in character than any other in organic chemistry. The proof that *m*-substitution in benzene derivatives is *sometimes* due to a general electrical effect of the first substituent suggests that *m*-direction may *always* be initiated in this way.

Among *m*-directive groups the only one which seems to present difficulty from this point of view is the sulphonic acid group. At first sight it is hard to reconcile the net negative charge of the sulphonic ion with an assumed tendency to attract electrons. It must be remembered, however, that sulphuric acid is a powerful dibasic acid and therefore $HS\bar{O}_4$, which may be written $HO{\cdot}S\bar{O}_3$, is evidently able to donate a proton to acceptor molecules, and this means that the $-S\bar{O}_3$ group, in spite of its charge, retains a high electron affinity. The phenomenon is doubtless connected with incomplete neutralisation of the charge of the sulphur atom by the distorted oxygen ions surrounding it (see the preceding communication) and with the partial neutralisation of the field of the oxygen ions by neighbouring kations and kationoid complexes.

The possibility that the sulphonic acid group is *m*-directive for the same reason that the ammonium-salt group is *m*-directive would become a probability if it could be shown that the effect is produced when a saturated carbon atom separates the sulphur atom from the benzene nucleus; we accordingly studied the nitration of toluene-ω-sulphonic acid. This substance is nitrated to a predominating extent in the *op*-positions, but the proportion of the

m-nitro-isomeride produced is much greater than that obtained in the nitration of toluene. This result confirms the view that the sulphonic ion group, $\bar{S}O_3$, has a higher electron affinity than has a hydrogen atom, and we may confidently attribute the *m*-substitution of benzenesulphonic acid to the occurrence of the condition $Ph\longrightarrow\bar{S}O_3$.

Toluene-ω-sulphonyl chloride, $Ph\longrightarrow CH_2\overset{(a)}{\longrightarrow}SO_2\overset{(b)}{\longrightarrow}Cl$, may be regarded as a sulphone in which the normal displacement (a) is reinforced by that (b) due to the chlorine atom. In harmony with our theory, the percentage of the *m*-isomeride formed in the nitration of this substance is much greater than that formed in the nitration of toluene-ω-sulphonic acid and considerably greater than that formed in the nitration of benzyl-*m*-nitrophenylsulphone.

The publication of Ingold, Ingold, and Shaw (this vol., p. 813), dealing with the nitration of substances of the form $CH_2Ph{\cdot}SO_2R$, appeared when our work was at a stage where the determinations of the proportion of *m*-isomeride formed in the nitrations had been completed. In view of it, the experimental section of this communication has been curtailed so that all repetition of description has been avoided. We carried out, for example, identifications of the products as nitrotoluene-ω-sulphonamides (compare Mohr, *Annalen*, 1883, **221**, 218; Purgotti and Monti, *Gazzetta*, 1900, **30**, ii, 254) and no further reference to this part of our work is deemed necessary.

EXPERIMENTAL.

Method of Estimation of the Proportion of m-*Isomeride formed in the Nitrations.*—Francis and Hill's method of bromination after reduction of the nitro-compounds with titanous chloride (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) has been found to be applicable to the sodium nitrotoluene-ω-sulphonates. Small corrections were applied for the deviations from the stoicheiometric relations found for sodium *o*-, *m*-, and *p*-nitrotoluene-ω-sulphonates.

Sodium *o*-nitrotoluene-ω-sulphonate was crystallised from semi-saturated brine and dried at 100—120° (Found: NaCl, 20·3; sodium nitrotoluenesulphonate estimated by titanous chloride, 79·4%). On reduction and bromination, the deviation from the theoretical value (in the volume of potassium bromate solution required for bromination) was − 0·4%. Sodium *m*-nitrotoluene-ω-sulphonate was crystallised from semi-saturated brine and dried at 130—140° (Found: NaCl, 7·1; sodium nitrotoluenesulphonate, 92·4%; deviation from theory on reduction and bromination, + 0·9%). The *o*-isomeride loses $1H_2O$ at 100°, but the *m*- and *p*-isomerides retain their water of crystallisation below 125°. Sodium

p-nitrotoluene-ω-sulphonate was crystallised from brine and dried at 140° (Found: NaCl, 1·9; sodium nitrotoluenesulphonate, 96·6%; deviation from theory on reduction and bromination, + 1·1%).

Some difficulty was experienced in obtaining satisfactory end-points in the final titrations with sodium thiosulphate, and this was overcome by using not too large an excess of bromine and by neutralising part of the acid after the liberation of iodine.

Nitration of Sodium Toluene-ω-sulphonate.—Sodium toluene-ω-sulphonate crystallised from 95% alcohol in lustrous leaflets, and the specimens employed were anhydrous and free from sodium chloride.

In a preliminary experiment, 20 g. of the salt were nitrated and 16·5 g. of washed sodium nitrotoluenesulphonates (dried at 100°) were obtained (Found: loss at 140° or H_2O, 6·0; NaCl, 8·6; sodium nitrotoluenesulphonates, 85·3%; *meta*, 20·2, 19·8, 18·5, 19·4%). The true yield was 57·6% and therefore the minimum value for the proportion of *m*-isomeride formed is 11—12%.

In attempts to improve the yield products were obtained containing sodium nitrate, which interfered seriously with the determinations. In subsequent experiments, the absence of nitrates was always confirmed.

Ultimately, the following nitration conditions were adopted: Sodium toluene-ω-sulphonate (10 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·5) at 0°, a further quantity of the acid (5 c.c.) being used to wash the sides of the container. Three hours from the commencement the ice-bath was removed and 1 hour later the solution was mixed with water (120 c.c.) and neutralised by means of sodium carbonate (20 g.), and after the addition of sodium chloride (30 g.) the liquid was heated until a clear solution resulted. The cooled liquid was kept at 0° for 3 hours and the separated solid was then washed twice with 15% brine (10 c.c.) and dried at 100° (Specimen A, 12·8 g.) (Found: H_2O, 4·9; NaCl, 10·0; sodium nitrotoluenesulphonate, 84·8%; *meta*, 11·7, 11·0, 10·6, 10·3, 9·6, 9·6%). The yield of sodium nitrotoluene-ω-sulphonates was therefore 88% and the minimum value for the proportion of *m*-isomeride formed is 9·2% (maximum, 21·2%). Another specimen (B) was prepared in the same manner (purity, 82%; true yield, 88%).

Nitration of Toluene-ω-sulphonic Acid.—The free acid (9 g.), prepared by Böhler's method (*Annalen*, 1870, **154**, 50), was treated exactly as described above for its sodium salt. The isolated, washed, and dried solids amounted to only 8·0 g. A further amount of sodium chloride (20 g.) was therefore added and 6·0 g. of the

mixed salts were obtained. The products were free from nitrates and were mixed (Found: H_2O, 3·3; NaCl, 39·9; sodium nitrotoluenesulphonates, 56·8%; *meta*, 14·2, 13·7, 14·2%). Here the true yield was 63·6% and the minimum value for the proportion of *m*-isomeride is 8·9%. We are unable to account for the variations in yield which were observed, but since the actual amount of the *m*-isomeride obtained was as great in this experiment (yield, 64%) as in the one previously described (yield, 88%), we may conclude that the proportion formed is greater in the nitration of the acid than in that of the salt. The point is not raised in the introduction, because it is hoped to follow up this indication by fresh experiments before the interesting theoretical implications are discussed.

Nitration of Toluene-ω-sulphonyl Chloride.—Toluene-ω-sulphonyl chloride (10 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·5) at 0°, a further amount of nitric acid (5 c.c.) being employed to wash the sides of the container. After 3 hours, the ice-bath was removed and 1 hour later the product was precipitated by water, collected, and boiled with a solution of sodium carbonate (11 g.) in water (100 c.c.) until no oil remained (about 1 hour). The liquid was filtered hot, sodium chloride (20 g.) introduced, and the mixture kept at 0° for 3 hours; the separated solid was then collected, washed twice with 15% brine (10 c.c.) at 0°, and dried at 100° (yield, 10·2 g.) (Found: H_2O, 5·7; NaCl, 12·3; sodium nitrotoluenesulphonates, 77·6%; *meta*, 44%). The yield was 63% and the minimum value for the proportion of *m*-isomeride formed is 28%. The specimen contained carbonate, and this probably accounts for the fact that the water, sodium chloride, and nitrocompounds determined totalled only 95·6%. Another nitration was carried out in exactly the same manner, but the alkaline solution was neutralised with hydrochloric acid and the sodium nitrotoluenesulphonates were salted out in two crops (mixed, 15·7 g.) (Specimen C) by means of sodium chloride (total, 50 g.) (Found: H_2O, 3·8; NaCl, 40·2; sodium nitrotoluenesulphonates, 55·8%; *meta*, 56, 54, 56, 56%). The true yield was 70·5% and the minimum value for the proportion of *m*-isomeride formed is 39% (maximum, 67·5%).

Comparison of these experiments shows that more efficient salting out increases the percentage of the *m*-isomeride in the product, and hence the true value for the *m*-isomeride content should be considerably greater than the minimum; it must also, of course, be much less than the maximum.

Estimation of the Proportions of the p-*Isomeride in Specimens A, B, and C.*—On heating at 100° with concentrated aqueous potassium hydroxide, the *o*- and *m*-nitrotoluene-ω-sulphonates

develop no coloration, whereas the *p*-isomeride gives a yellowish-orange solution. Attempts to apply this reaction in a colorimetric method gave unintelligible results until it was found that the colour produced by the *p*-isomeride is more intense in the presence of the *o*-isomeride and still more intense in the presence of the *m*-isomeride. The *o*- and *m*-isomerides give no coloration when mixed and heated with aqueous potassium hydroxide.

Solutions were made up to contain 1·0% of the pure *o*-, *m*-, and *p*-isomerides and of the nitro-compounds in specimens A, B, and C. 10 C.c. of one of these solutions or of a mixture of them were mixed with 25 c.c of a solution of potassium hydroxide (100 g.) in water (100 c.c.) and heated in a bath of boiling water for about 2 hours. All the comparisons were direct under identical conditions, and in addition to the determination of the intensity of the colour the rapidity of its appearance afforded valuable guidance. In making up the standards, the ascertained percentage of the *m*-isomeride in the specimen to be tested was introduced and kept constant, the proportions of the *p*- and *o*-isomerides being varied.

In the case of specimen C, the colour was practically identical with that of a standard made from 5·5 c.c. of the *m*-isomeride solution and 4·5 c.c. of the *p*-isomeride solution and was distinctly stronger than that obtained from the standard—*m*-, 5·5; *p*-, 4·0; *o*-, 0·5 c.c. The colours were estimated after dilution of the solutions to 40 c.c. by means of the Zeiss "Stufenphotometer." The specimen C, obtained in 70·5% yield from the nitration of toluene-ω-sulphonyl chloride, does not, therefore, contain an appreciable amount (<5%) of the *o*-isomeride.

No difference could be detected in the behaviour of the specimens A and B when a direct comparison was made; most of the experiments were therefore made with B, because a larger quantity of this specimen was available. A series of comparisons with standards showed that the colour derived from B was more intense than that from the standard—*m*-, 1·0; *p*-, 4·5; *o*-, 4·5 c.c., and less intense than that from the standard—*m*-, 1·0; *p*-, 5·0; *o*- 4·0 c.c.

The actual intensity measurements of these and four other standards compared with the solution from B were used to construct a graph, by means of which the solution exactly equivalent to the B solution was found to be—*m*-, 1·0; *p*-, 4·8; *o*-, 4·2 c.c. This was experimentally confirmed with solutions made up from quantities weighed on a micro-balance.

A specimen was made by admixture of the *o*-, *m*-, and *p*-isomerides and sodium chloride that contained 82% of the pure sodium nitrotoluene-ω-sulphonates (*m*-, 10; *o*-, 40; *p*- 50%) and was found

in numerous quantitative trials under different conditions to resemble B closely in behaviour. The colours were developed a very little the more rapidly with the artificial mixture. Finally, the specimen A was reproduced on the same basis and with the same results.

The colour reactions observed with alkaline solutions also guarantee the absence of sodium dinitrotoluene-ω-sulphonates. A specimen of the latter (probably the 2 : 4-dinitro-derivative) was prepared by nitration of sodium *o*-nitrotoluene-ω-sulphonate with a hot mixture of sulphuric and nitric acids. The sodium salt crystallised in colourless leaflets and developed a green colour with cold, dilute aqueous sodium hydroxide; on heating, an intense bluish-green solution was obtained.

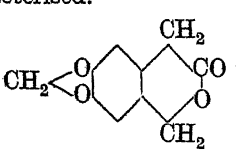
The authors wish to thank the Advisory Council of the Department of Scientific and Industrial Research for a grant that enabled one of them to take part in the investigation.

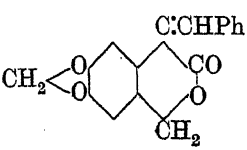
THE UNIVERSITY, MANCHESTER. [*Received, September 12th*, 1927.]

CCCLXXII.—*A New Synthesis of Hydrastic Acid.*

By THOMAS STEVENS STEVENS and MARY CARRICK ROBERTSON.

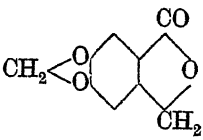
IN the course of recent synthetic work, the lactone (I) was obtained by the action of formaldehyde on homopiperonylic acid, and its structure confirmed by oxidising it to 4 : 5-methylenedioxyhomophthalic acid (Stevens, this vol., p. 178). It was further considered desirable to attempt the conversion of (I) into hydrastic acid, both on account of the interest attaching to a synthesis of that important substance, and also because the homophthalic acid is not readily characterised.

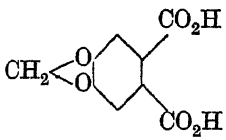
(I.) 

 (II.)

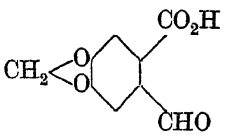
The compound (I) was condensed with benzaldehyde in presence of piperidine to form the lactone (II) of α-(6-*hydroxymethylpiperonyl*)-*cinnamic acid*. Oxidation with neutral permanganate converted this into 4 : 5-*methylenedioxyphthalide* (III), which was further oxidised in alkaline solution to hydrastic acid (IV). The substances

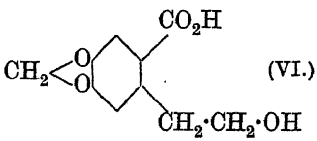
(III) and (IV) are clearly the "methylenedioxy-analogues" of *m*-meconin and *m*-hemipinic acid, and it was hoped that it would

(III.) 

(IV.) 

be possible to complete the series by oxidising (III) to the aldehydo-acid (V), analogous to *m*-opianic acid, but this could not be accomplished.

(V.) 

(VI.) 

The hydroxy-acid derived from the lactone (I) lactonises spontaneously when liberated from its salts, whereas that derived from (III), like many derivatives of *o*-hydroxymethylbenzoic acid, is comparatively stable. This greater stability of the γ-hydroxy-acids relatively to the δ-, as compared with the opposite behaviour of simple aliphatic compounds, is significant in view of von Braun's suggestion that in the formation of cyclic structures two carbon atoms of a benzene ring are sterically more nearly equivalent to one methylene group than to two (*Ber.*, 1925, **58**, 2765; 1927, **60**, 1257). On the other hand, 6-β-hydroxyethylpiperonylic acid (VI) (Perkin, J., 1890, **57**, 1020) and β-*o*-hydroxyphenylpropionic acid are fairly stable. The relative stabilities of these three δ-hydroxy-acids are in striking contrast to those of the δ-amino-acids prepared by von Braun and Reich (*Annalen*, 1925, **445**, 225), who observed that the lactam of *o*-aminomethylphenylacetic acid, analogous to (I), was *less* readily formed than those of the isomeric β-*o*-aminophenylpropionic and *o*-β-aminoethylbenzoic acids.

Experimental.

α-(6-*Hydroxymethylpiperonyl*)*cinnamolactone* (II).—The lactone (I) (10 g.) is dissolved in hot benzaldehyde (15 c.c.), piperidine (8—10 drops) added, and the mixture heated at 120° for 2 hours. The melt is dissolved in boiling acetic acid, and the solid (12 g.), which separates on cooling, recrystallised from alcohol or acetic acid. It forms pale yellow needles, m. p. 190—192°, fairly soluble in hot acetic acid and sparingly soluble in alcohol, and gives an intensely orange solution in concentrated sulphuric acid (Found: C, 72·9; H, 4·3. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%). It dis-

solves slowly in boiling aqueous alkali to a colourless solution: on acidification a colourless acid separates, which passes back into the lactone on being heated with dilute acids.

4 : 5-*Methylenedioxyphthalide* (III).—A solution of the lactone (II) (10 g.) in warm acetone (230—300 c.c.) is cooled (any crystallisation being disregarded), and stirred during the gradual addition of potassium permanganate (13 g.) and magnesium sulphate (13 g.) in warm concentrated aqueous solution. The mixture is boiled and filtered; much of the product then separates on cooling, and more may be obtained from the manganese sludge (5 g. in all). Methylenedioxyphthalide is soluble in about 100 parts of boiling water, and crystallises in white needles, m. p. 188—189°, which sublime readily without decomposition at about 150—160°. The sublimate consists principally of stout, short prisms which show the same m. p. as the original material and are reconverted into the needles on crystallisation from water (Found: C, 60·6; H, 3·7. $C_9H_6O_4$ requires C, 60·6; H, 3·4%). Attempts to oxidise the substance to the aldehydo-acid (V) with manganese or lead dioxide and sulphuric or acetic acid, or with chromic anhydride in acetic anhydride, were not successful.

6-*Hydroxymethylpiperonylic Acid.*—The phthalide (III) is not attacked by cold carbonates, but rapidly dissolves in hot sodium hydroxide solution, and the hydroxy-acid is precipitated in minute crystals when the cold solution is acidified. It melts indefinitely at about 140—150°, quickly resolidifies, and then melts at the m. p. of the lactone (Found: *M*, by titration, 193. $C_9H_8O_5$ requires *M*, 196). The acid is readily soluble in hot water and crystallises unchanged on rapid cooling; boiling dilute mineral acids reconvert it at once into the lactone. The *silver* salt forms colourless, microscopic prisms which are sparingly soluble in boiling water (Found: Ag, 35·8. $C_9H_7O_5Ag$ requires Ag, 35·6%).

Hydrastic Acid (IV).—The phthalide (III) was dissolved in dilute alkali solution and oxidised in the cold with a moderate excess of aqueous potassium permanganate. On acidification of the filtrate from the manganese dioxide, hydrastic acid, m. p. 175° (decomp.), crystallised in a yield of more than 50% of the theoretical. It was characterised by conversion into the methylimide, m. p. 228°, and by analysis of the silver salt (Found: Ag, 51·0. Calc., Ag, 50·9%).

UNIVERSITY OF GLASGOW. [*Received, September 15th*, 1927.]

CCCLXXIII.—*The Action of Tolylhydrazines upon Dihydroxytartaric Acid.*

By Frederick Daniel Chattaway and William Gerald Humphrey.

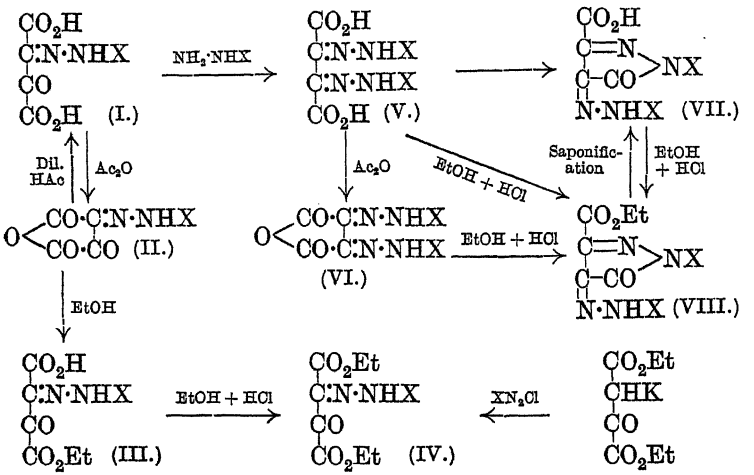
Although the osazones of dihydroxytartaric acid have been thoroughly investigated, its monohydrazones have never been prepared in a pure condition. Gnehm and Benda (*Annalen*, 1897, 299, 100) showed that the action of *p*-nitrophenylhydrazine upon excess of dihydroxytartaric acid yielded the pure osazone with no trace of a monohydrazone, whilst phenylhydrazine gave a mixture of the monohydrazone and osazone, which they did not separate into the two constituents. The action of halogen-substituted phenylhydrazines results in the formation of similar mixtures (this vol., p. 1323).

The action of *o*- and *p*-tolylhydrazines upon dihydroxytartaric acid differs from that of other hydrazines in that pure monohydrazones are readily obtained. These are well-crystallised, yellow solids, which, like the corresponding osazones, are converted into deep red acid anhydrides on heating with acetic anhydride. On crystallising these anhydrides from dilute acetic acid, the original hydrazones are re-formed; similarly, on crystallising the anhydrides from anhydrous alcohol, half-esters are formed. The second carboxyl group undergoes esterification only with difficulty, requiring prolonged boiling with alcohol containing hydrogen chloride; the diethyl ester thus formed may also be obtained by coupling diazotised toluidine with the potassium derivative of ethyl oxalacetate.

The most important property of the osazones of dihydroxytartaric acid is the ease with which they lose a molecule of water to give pyrazoline derivatives. This property is completely absent from the monohydrazones, and all attempts to cause pyrazoline ring formation have been unsuccessful.

The *o*- and *p*-tolylosazones of dihydroxytartaric acid behave in the normal manner. They are sparingly soluble substances which cannot be crystallised unchanged from any solvent. They are converted into deep red anhydrides by heating with acetic anhydride, and into hydrazones of diketopyrazolinecarboxylic acids by crystallisation from acetic acid or by acidification of their sodium salts. In the former reaction, varying amounts of the isomeric anhydrides are simultaneously produced. These pyrazoline derivatives undergo esterification with difficulty and their esters are more easily obtained from the corresponding osazone.

The following scheme represents the reactions, X denoting the tolyl group:



EXPERIMENTAL.

Diketosuccinic acid o-*tolylhydrazone* (I) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1 : 1) to a solution of 16 g. of *o*-tolylhydrazine hydrochloride (1 mol.) in 1000 c.c. of very dilute hydrochloric acid (1 : 100). The *hydrazone* separated slowly as a deep yellow, crystalline powder, which was filtered off after 3—4 hours and crystallised from 75% acetic acid, in which it was moderately easily soluble and from which it separated in yellow, elongated, flat prisms, m. p. 192° (decomp.) (Found: N, 11·2. $C_{11}H_{10}O_5N_2$ requires N, 11·2%).

This hydrazone shows no tendency to lose water to form a pyrazoline derivative. It dissolves readily in hot sodium hydroxide solution and is reprecipitated on acidification. On boiling with acetic acid, partial conversion into the anhydride occurs, whilst boiling with alcohol containing hydrogen chloride causes esterification only.

Anhydrodiketosuccinic Acid o-*Tolylhydrazone* (II).—The hydrazone (I) was added to boiling acetic anhydride until no more would dissolve. A clear, deep red solution was thus obtained which on cooling deposited the *anhydride* in long, red, glistening prisms, m. p. 208° (decomp.) (Found: N, 12·2. $C_{11}H_8O_4N_2$ requires N, 12·1%).

Ethyl Hydrogen Diketosuccinate o-*Tolylhydrazone* (III).—The

above anhydride was boiled with anhydrous alcohol and the yellow solution thus obtained, on cooling, deposited the half-ester in yellow, irregular, thin plates, m. p. 115° (Found: N, 9·9. $C_{13}H_{14}O_5N_2$ requires N, 10·1%).

The half-ester may also be prepared by boiling the hydrazone (I) with alcohol containing 5% of dry hydrogen chloride for ½ hour.

A definite formula cannot be assigned to this ester, as there is nothing to indicate which of the two carboxyl groups is esterified. The product appears not to be a mixture; its melting point is not changed by recrystallisation, and the fact that the second group can be esterified only with great difficulty points to a particular one being concerned in the first reaction.

Ethyl Diketosuccinate o-*Tolylhydrazone* (IV).—Although one carboxyl group of diketosuccinic acid *o*-tolylhydrazone is readily esterified, the diethyl ester was formed only by boiling the half-ester for 12 hours with alcohol saturated with dry hydrogen chloride. A certain amount of decomposition and tar formation occurred, and a dark brown solution was obtained, which on cooling deposited the *diethyl* ester in bright yellow, hexagonal plates or flattened prisms, m. p. 90° (Found: N, 9·1. $C_{15}H_{18}O_5N_2$ requires N, 9·15%).

The same ester was prepared by adding slowly a cold aqueous solution of *o*-toluenediazonium chloride (1 mol.) to an aqueous solution of the potassium derivative of ethyl oxalacetate (1 mol.), cooled in a freezing mixture. A sticky, red mass separated, from which, by crystallisation from alcohol, ethyl diketosuccinate *o*-tolylhydrazone was obtained, identical with that prepared by direct esterification.

Diketosuccinic acid o-*tolylosazone* (V) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1 : 1) to a solution of 32 g. of *o*-tolylhydrazine (2 mols.) in 1500 c.c. of dilute hydrochloric acid (1 : 100). The mixture was stirred for 6 hours and heated at 80° for 2 hours. The *osazone* was filtered off without previous cooling, repeatedly washed with boiling water, and dried at 110°. It was thus obtained as an orange powder, m. p. 170° (decomp.) (Found: N, 15·6. $C_{18}H_{18}O_4N_4$ requires N, 15·8%).

Anhydrodiketosuccinic Acid o-*Tolylosazone* (VI).—The osazone (V) was added to boiling acetic anhydride until no more would dissolve. On cooling, the *anhydride* separated in long, glistening, red prisms, m. p. 198° (decomp.) (Found: N, 16·6. $C_{18}H_{16}O_3N_4$ requires N, 16·7%).

4 : 5-*Diketo*-1-o-*tolylpyrazoline*-3-*carboxylic acid* 4-o-*tolylhydrazone* (VII) is formed together with the isomeric anhydride (VI) on crystallising the osazone (V) from acetic acid. It is, however,

best obtained by acidifying the orange-coloured solution produced by dissolving the osazone in hot 10% sodium hydroxide solution; the *tolylhydrazone* thus obtained separates from acetic acid, in which it is sparingly soluble, in very small, yellow prisms, m. p. 229° (decomp.) (Found: N, 16·45. $C_{18}H_{16}O_3N_4$ requires N, 16·7%).

Its *ethyl* ester (VIII), obtained by boiling the osazone (V), the anhydride (VI), or the pyrazolone (VII) with alcohol containing 5% of dry hydrogen chloride, crystallises from alcohol, in which it is easily soluble, in long, orange-red prisms, m. p. 145° (Found: N, 15·5. $C_{20}H_{20}O_3N_4$ requires N, 15·4%).

The following derivatives of *p*-tolylhydrazine were similarly prepared.

Diketosuccinic acid p-*tolylhydrazone* (I) is moderately easily soluble in 75% acetic acid, from which it separates in orange-yellow octahedra, m. p. 190° (decomp.) (Found: N, 11·3%). The *anhydride* (II) crystallises from acetic anhydride in deep red, elongated prisms, m. p. 192° (decomp.) (Found: N, 12·1%). The *half-ester* (III) is easily soluble in alcohol, from which it separates in lemon-yellow, slender prisms, m. p. 112° (Found: N, 10·05%).

Diketosuccinic acid p-*tolylosazone* (V) was obtained as a soft, orange-red powder, m. p. 175° (decomp.) (Found: N, 15·65%). The *anhydride* (VI) forms red, elongated prisms, m. p. 230° (decomp.) (Found: N, 16·5%).

4 : 5-*Diketo*-1-p-*tolylpyrazoline*-3-*carboxylic acid* 4-p-*tolylhydrazone* (VII) is sparingly soluble in acetic acid, from which it separates in very small, pale yellow prisms, m. p. 233° (decomp.) (Found: N, 16·7%). Its *ethyl* ester (VIII) is easily soluble in alcohol, from which it separates in orange-red, slender prisms, m. p. 143° (Found: N, 15·55%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, October 11th*, 1927.]

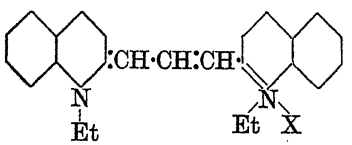
CCCLXXIV.—*A General Method for the Preparation of Carbocyanine Dyes.*

By FRANCES MARY HAMER.

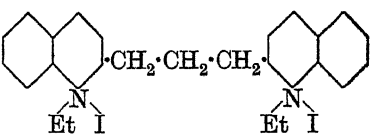
SINCE 1920, when the term "carbocyanine" was first applied to pinacyanol and similar dyes (Mills and Pope, *Phot. J.*, 1920, **44**, 253), other types of compounds have been discovered which, from their structure and properties, should be included under the same name. Before describing the present general method of preparing carbocyanines, it seems desirable to summarise these various types

and the methods which have hitherto been employed in making them.

The most important carbocyanine dye is 1 : 1′-diethyl-2 : 2′-carbocyanine halide (I), which, under the trade name of pinacyanol, is a well-known photographic sensitiser. Hitherto the best way of preparing it has consisted in adding formaldehyde and then alkali to a boiling alcoholic solution of a quinaldinium salt in the presence of a quinolinium salt, but the yield of pure dye is at most only 21% of that theoretically possible. The part played by formaldehyde may be taken by a trihalogenomethane (D.R.-P., 200,207/1908), or the methenyl residue may be provided by di-*o*-formylethylaminodiphenyl disulphide, reacting with quinaldine ethonitrate in pyridine solution (Mills and Braunholtz, J., 1923, **123**, 2804). König obtained pinacyanol by the condensation of quinaldine ethiodide with ethyl orthoformate in the presence of acetic anhydride (*Ber.*, 1922, **55**, 3293), but his claim to a 50% yield could not be confirmed (Hamer, J., 1925, **127**, 211). Finally, the dye has been derived from methylenediquinaldine diethiodide (II) by the action of alkali

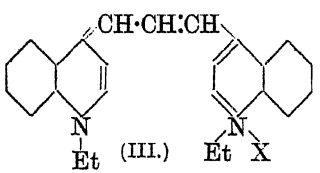


(I.)

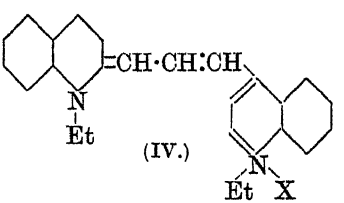


(II.)

in the presence of a quinolinium salt (Hamer, J., 1923, **123**, 246). The establishment of the constitution of pinacyanol (Mills and Hamer, J., 1920, **117**, 1550) led to the prediction of two similar groups of carbocyanines, possessing respectively a 4 : 4′- and a 2 : 4′-linking (III and IV) in place of the original 2 : 2′-linking. Mills and Braunholtz (*loc. cit.*) prepared a dye of the first type (III)



(III.)

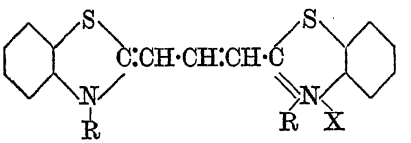


(IV.)

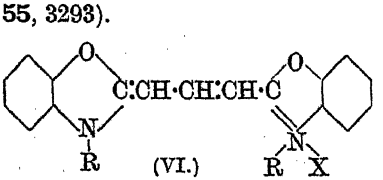
from lepidine ethonitrate by the action of the disulphide and pyridine, and showed the corresponding iodide, obtainable in 15% yield, to be identical with " kryptocyanine," which had previously been prepared, in 9% yield, by treating an alcoholic solution of lepidine ethiodide with alkali and formaldehyde or chloroform (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661). Mills

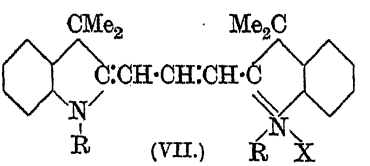
and Odams similarly synthesised the 2 : 4′-isomeride (IV) by the action of the disulphide on the ethonitrates of quinaldine and lepidine, and proved "dicyanine" to be a dye of this kind (J., 1924, **125**, 1913).

Besides these three closely related classes of carbocyanines, analogous dyes are obtained when the quinoline nuclei are replaced by other basic nuclei. Mills has shown that the dyes formed by the action of ammonia on the quaternary salts of 1-methylbenzthiazole and benzthiazole (Hofmann, *Ber.*, 1887, **20**, 2262) result in better yield (19%) when the salts are heated in pyridine solution, and has proved that they have formula (V) (J., 1922, **121**, 455). Substances of the same class were prepared by König and Meier,

(V.) 

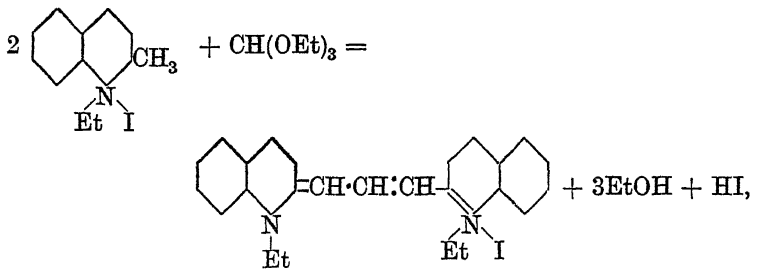
by condensation of 1-methylbenzthiazole methohalide with ethyl orthoformate, or anhydrous sodium formate, in nitrobenzene solution; they mention that the reaction proceeds equally well in acetic anhydride or pyridine solution (*J. pr. Chem.*, 1925, **109**, 324). Repetition of the preparation of the methobromide in nitrobenzene solution, or of the methiodide in acetic anhydride solution, has been found to give unsatisfactory results. By heating 1-methylbenzoxazole methiodide with ethyl orthoformate in the presence of nitrobenzene or acetic anhydride, König and Meier prepared a dye of a new type (VI) (*loc. cit.*), whilst König prepared another class of carbocyanine (VII) by treatment of a 2 : 3 : 3-trimethylindoleninium salt with ethyl orthoformate and acetic anhydride (*Ber.*, 1924, **55**, 3293).


(VI.)


(VII.)

As regards the nomenclature of these last three groups of carbocyanine dyes, the term *thiocarbocyanine* is preferred to the name carbothiocyanine (Mills, *loc. cit.*), as being more consistent with the terms thio*iso*cyanine (Braunholtz and Mills, J., 1922, **121**, 2004), thio*pseudo*cyanine (Mills and Braunholtz, *loc. cit.*), and pyridocarbocyanine (*ibid.*). It is proposed that the dyes (VI) and (VII), derived from benzoxazole and indolenine, be named *oxacarbocyanines* and *indocarbocyanines* respectively.

Now the equation representing the reaction of quinaldine ethiodide



with ethyl orthoformate suggests that the pinacyanol condensation would be favoured by the use of a basic solvent. Boiling pyridine proved in fact to serve excellently, and to its use is attributable the whole success of the present method. The only precaution necessary is that of drying the solvent, whilst about four times the calculated quantity of ester should be taken. Three 2 : 2′-carbocyanines have been prepared by the pyridine method, the yields of pure product varying from 70 to 79%, and the method was subsequently applied to the preparation of carbocyanines of the other five classes. With the 2 : 4′-carbocyanines, the yield of crude material is higher and the labour involved is less than in any other published method of preparing dicyanines; their separation, by fractional crystallisation, from the 2 : 2′- and 4 : 4′-isomerides was not, however, carried out. The success of the method is especially striking in the case of the 4 : 4′-carbocyanines, the yields being 36 to 43% of the theoretical. In the preparation of 1 : 1′-diethyl-4 : 4′-carbocyanine iodide, there is formed in addition about half its amount of another dye, which may readily be isolated by virtue of its slight solubility. Its properties show it to be identical with " neocyanine," which has been described as a by-product in the preparation of kryptocyanine by the formaldehyde method, and which is a powerful sensitiser for the deep red and infra-red (Dundon, Schoen, and Briggs, *J. Opt. Soc. Amer.*, 1926, **12**, 397). The pyridine method is at its best in the case of the thiocarbocyanines, giving between 79 and 83% yields of pure dyes; with the oxacarbocyanines the yields are about 40% and with the indocarbocyanines about 70% of those theoretically obtainable.

It is concluded that the introduction of pyridine as solvent converts the synthesis of carbocyanines, by condensation of ethyl orthoformate with quaternary salts containing reactive methyl groups, into an excellent practical and general method of preparation; this is not only the simplest method to apply, but gives, in any and every instance, the best yield obtainable. The following

carbocyanines are now described for the first time : 6 : 6′-*dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine iodide* and *bromide*, 1 : 1′-*dimethyl*-4 : 4′-*carbocyanine iodide*, 1 : 1′-*diallyl*-4 : 4′-*carbocyanine iodide*, 2 : 2′-*diallylthiocarbocyanine bromide*, 2 : 2′-*diethyloxacarbocyanine iodide*, and 3 : 3 : 3′ : 3′-*tetramethyl*-1 : 1′-*diethylindocarbocyanine iodide*.

Mr. O. F. Bloch has examined the absorption spectra of all the dyes in alcoholic solution and tested their sensitising action, both by bathing plates in a solution and by adding the dye to the emulsion before coating. He has found that the indocarbocyanines and oxacarbocyanines are, like other cyanine dyes, photographic sensitisers, and it seems remarkable that their photographic properties have not previously been recorded. In the experimental section of this paper the photographic action is described only in those instances where this has not previously been done.

So far no carbocyanine containing two pyridine nuclei has been isolated, though Mills and Braunholtz (*loc. cit.*) attributed to a 2 : 2′-carbocyanine of this type absorption bands which they detected in the pyridine reaction mixture of 2-methylpyridine ethonitrate and di-*o*-formylethylaminodiphenyl disulphide. It is now found that a 2 : 2′-pyridocarbocyanine is not formed by condensation of 2-methylpyridine ethiodide with ethyl orthoformate in the presence of boiling pyridine, a negative result which is curious in view of the readiness with which 2-methylpyridine quaternary salts condense with *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736) and with *p*-dimethylaminobenzaldehyde (Mills and Pope, J., 1922, **121**, 946).

Experimental.

1 : 1′-*Diethyl*-2 : 2′-*carbocyanine Iodide*.—Quinaldine ethiodide (5 g.; 2 mols.), ethyl orthoformate (5·5 c.c.; 4 mols.), and pyridine (20 c.c.), which had been dried by being left over barium oxide and subsequent decantation, were boiled under reflux for 3 hours; crystals then separated (yield 78%). After recrystallisation from dilute spirit, the yield was 70%. The dye was dried under reduced pressure at 100—120° and an iodine determination was made by the method of Carius; these methods of drying and analysis were used in all cases, except where otherwise stated (Found : I, 26·2. Calc. for $C_{25}H_{25}N_2I$: I, 26·4%).

6 : 6′-*Dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine Iodide*.—By heating 2 : 6-dimethylquinoline (5 g.; 1 mol.) and allyl iodide (3·4 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours, extracting the product with ether, and recrystallising the residue from spirit, a 72% yield of 2 : 6-*dimethylquinoline alliodide* was obtained, in yellow crystals,

m. p. 198—199° (decomp.) (Found: I, 39·2. $C_{14}H_{16}NI$ requires I, 39·05%). The condensation of the alliodide (5 g.) with ethyl orthoformate was carried out as in the previous preparation and the product was washed with ether (yield 82%) and recrystallised from methyl alcohol (yield, 71%). It melts with decomposition at 280—281° (Found: I, 23·5. $C_{29}H_{29}N_2I$ requires I, 23·85%). In spirit solution there are absorption maxima at λ 5700 Å. and λ 6200, of which the latter is the stronger. When the dye is added to the emulsion the sensitising maxima lie at λ 5800 and λ 6450 and there is considerable fog. The fog is less when the plate is bathed in a solution of the dye, and the sensitising action is considerably greater, the principal band now extending from λ 6200 to λ 7300.

6 : 6′-*Dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine Bromide*.—A 76% yield of 2 : 6-*dimethylquinoline allobromide* is obtained by heating 2 : 6-dimethylquinoline (7 g.; 1 mol.) and allyl bromide (6·2 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours and recrystallising the product from absolute alcohol. It is a colourless solid, m. p. 214—215° (decomp.) (Found: Br, 28·9. $C_{14}H_{16}NBr$ requires Br, 28·7%). Its condensation with ethyl orthoformate in the presence of pyridine gave an 84% yield of carbocyanine (14·6 g.) and on recrystallisation from methyl alcohol a 79% yield of pure dye. This forms green and gold crystals, m. p. 281—282° (decomp.) (Found: Br, 16·5. $C_{29}H_{29}N_2Br$ requires Br, 16·5%).

1 : 1′-*Dimethyl*-4 : 4′-*carbocyanine Iodide*.—This compound is mentioned in the literature (Adams and Haller, *loc. cit.*), but none of its properties has been recorded. After condensation of lepidine methiodide (1 g.) with ethyl orthoformate in the presence of pyridine, the reaction mixture was poured into water; a 71% yield of crude product then resulted. From methyl alcohol it separated in minute, bright green crystals (yield 38%), m. p. 290—295° (decomp.) (Found: I, 28·0. $C_{23}H_{21}N_2I$ requires I, 28·1%). The dye shows an absorption maximum at λ 7150. The sensitising action towards plates on bathing is poor and is accompanied by veil; the single sensitising band has its maximum at λ 7500. When the dye is added to the emulsion, the sensitising action is less but the fog greater.

1 : 1′-*Diethyl*-4 : 4′-*carbocyanine Iodide* (*Kryptocyanine*).—After the condensation of lepidine ethiodide with ethyl orthoformate in the usual way, the reaction mixture was cooled and filtered (0·89 g. removed); on addition of water to the filtrate, the kryptocyanine was precipitated (2·23 g., *i.e.*, 56% of the theoretical yield). The kryptocyanine was recrystallised from spirit (150 c.c.); the yield (1·67 g.) was then 42% (Found: I, 26·4. Calc. for $C_{25}H_{25}N_2I$: I, 26·4%). The less soluble neocyanine iodide also was recrystallised

from spirit (1000 c.c.; 0·72 g. obtained). When heated, it melts with decomposition at 286°.

1 : 1′-*Diallyl*-4 : 4′-*carbocyanine Iodide*.—Lepidine (3·9 c.c.; 1 mol.) and allyl iodide (3·2 c.c.; 1·2 mols.) were heated in a sealed tube at 100° for 2 days. The *lepidine alliodide* was recrystallised twice from dry spirit, charcoal being used once (Found: I, 40·8. $C_{13}H_{14}NI$ requires I, 40·8%). The condensation product from lepidine alliodide (1 g.) and ethyl orthoformate was precipitated as a tar on the addition of ether to the pyridine reaction liquid. Rapid crystallisation from a little methyl alcohol gave a 43% yield of green crystals, but the carbocyanine was unstable and decomposed on prolonged boiling with the solvent. When heated, decomposition began at about 150° (Found: I, 25·6. $C_{27}H_{25}N_2I$ requires I, 25·2%). The maximum absorption in spirit solution is at λ 7150. On a bathed plate, the dye confers a strong sensitisation band with its maximum at λ 7550. The band occupies the same position when the dye is added to the emulsion, but is in this case much weaker.

2 : 2′-*Dimethylthiocarbocyanine Iodide*.—Repetition of the preparation using ethyl orthoformate and acetic anhydride gave only 17% and 9% yields of crude and recrystallised dye respectively. By the new method, 1-methylbenzthiazole methiodide (4 g.; 2 mols.), pyridine (40 c.c.), and ethyl orthoformate (4·6 c.c.; 4 mols.) were boiled for an hour. The thiocarbocyanine (yield, 95%) was recrystallised from dilute spirit and obtained in 74% yield. Melting with decomposition occurs at about 280°; König and Meier (*loc. cit.*) give m. p. 254° (Found: I, 27·1. Calc. for $C_{19}H_{17}N_2IS_2$: I, 27·3%).

2 : 2′-*Diethylthiocarbocyanine Iodide*.—This dye was similarly prepared from 1-methylbenzthiazole ethiodide (2 g.), and recrystallised from methyl alcohol (yield, 82%); m. p. 264—265° (decomp.); Mills (*loc. cit.*) gives m. p. 269° (decomp.) (Found: I, 25·6. Calc. for $C_{21}H_{21}N_2IS_2$: I, 25·8%).

2 : 2′-*Diallylthiocarbocyanine Bromide*.—By heating 1-methylbenzthiazole (6·3 g.; 1 mol.) with allyl bromide (3·5 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours and recrystallising the product from spirit, 1-*methylbenzthiazole allobromide* was obtained in almost colourless crystals (yield, 68%), m. p. 202° (decomp.) (Found: Br, 29·8. $C_{11}H_{12}NBrS$ requires Br, 29·6%). The crude dye (yield, 95%), obtained on condensation of 1-methylbenzthiazole allobromide (2 g.) with ethyl orthoformate, was recrystallised from methyl alcohol; the pure thiocarbocyanine (yield, 79%) forms purple crystals, m. p. about 260° (decomp.) (Found: Br, 17·0. $C_{23}H_{21}N_2BrS_2$ requires Br, 17·0%). In spirit solution, the stronger absorption band has its maximum at λ 5600 and the weaker at λ 5220. As used in the emulsion, the dye is a powerful sensitiser;

there is a strong band with its maximum at λ 6000 and a weaker one with a maximum at λ 5450. It acts as an excellent sensitiser when plates are bathed in its solution, the sensitisation being almost uniform up to λ 6200 and decreasing to zero at λ 6800; there is a slight gap at λ 4900.

2 : 2′-*Dimethyloxacarbocyanine Iodide.*—1-Methylbenzoxazole could not be obtained by interaction of *o*-aminophenol and ethyl acetate (Niementowski, *Ber.*, 1897, **30**, 3062), but was prepared by Ladenburg's method (*Ber.*, 1876, **9**, 1524). The methiodide, after being washed with dry ether as described by Clark (J., 1926, 232), was rapidly recrystallised from absolute alcohol; the colourless crystals obtained were washed with ether and dried in a vacuum desiccator before analysis (Found: I, 46·1. Calc. for $C_9H_{10}ONI$: I, 46·15%). M. p. 196° (decomp.) as recorded by Clark; König and Meier (*loc. cit.*) give m. p. 200°. 1-Methylbenzoxazole methiodide (2 g.; 2 mols.), ethyl orthoformate (3·0 c.c.; 4 mols.), and pyridine (20 c.c.) were boiled for an hour. The dye (yield, 57%) was recrystallised from absolute alcohol (yield, 40%). The yield is about half as great when acetic anhydride is used as solvent in the condensation. The oxacarbocyanine has m. p. 275—277° (decomp.); König and Meier give m. p. 259° (Found: I, 29·2. Calc. for $C_{19}H_{17}O_2N_2I$: I, 29·4%). The absorption maxima in spirit solution lie at λ 4850 and λ 4600, of which the former is the stronger. When added to the emulsion, the dye confers a region of extra sensitivity with a maximum at λ 5100. Both in this case and with the bathed plate the sensitisation curve is very uniform, reaching to λ 5700 for moderate exposures.

2 : 2′-*Diethyloxacarbocyanine Iodide.*—1-*Methylbenzoxazole ethiodide* was prepared by heating 1-methylbenzoxazole (5·5 g.; 1 mol.) and ethyl iodide (4·0 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours. After extraction with dry ether, the crude product was rapidly recrystallised from absolute alcohol, washed with ether, and dried for analysis in a vacuum desiccator (yield, 74%); the colourless crystals thus obtained had m. p. 195—197° (decomp.) (Found: I, 43·7. $C_{10}H_{12}ONI$ requires I, 43·9%). Condensation of the ethiodide (8 g.) with ethyl orthoformate gave 2 : 2′-*diethyloxacarbocyanine iodide* (yield, 57%), which crystallised from pyridine, in 38% yield, in red crystals with a blue reflex; m. p. 277—279° (decomp.) (Found: I, 27·5. $C_{21}H_{21}O_2N_2I$ requires I, 27·6%). The absorption maxima in spirit solution are at λ 4600 and λ 4850, of which the latter is the stronger. For bathing plates the dye acts as a powerful sensitiser, extending the normal sensitivity by a band which shows a maximum at λ 5150. Its action is weaker when it is added to the emulsion.

1 : 3 : 3 : 1′ : 3′ : 3′-*Hexamethylindocarbocyanine Iodide.*—In this instance the yield obtained by using acetic anhydride as solvent is equal to that which results when pyridine is employed. 2 : 3 : 3-Trimethylindolenine methiodide (2 g.; 2 mols.), pyridine (20 c.c.), and ethyl orthoformate (3·0 c.c.; 4 mols.) were boiled for an hour and the reaction mixture was poured into water. The crude product (yield, 78%) gave on recrystallisation from dilute or dry spirit, acidified with hydrogen iodide, a 66% yield of beautifully crystalline dye, but the iodine content was invariably low (*e.g.*, a specimen which had been dried in a vacuum desiccator gave C, 60·6; H, 6·5; I, 24·0. Calc. for $C_{25}H_{29}N_2I$: C, 61·95; H, 6·0; I, 26·2%. $C_{25}H_{29}N_2I,C_2H_5{\cdot}OH$ requires C, 61·1; H, 6·65; I, 23·9%). The indocarbocyanine has m. p. about 228° (decomp.); König (*loc. cit.*) gives m. p. 229° (decomp.). The absorption maxima lie at λ 5120 and λ 5480. When added to the emulsion, the dye gives very clean plates and shows fair sensitising action; the maxima lie at λ 5320 and λ 5720. When plates are bathed in a solution of the dye, the sensitisation is very powerful, and maxima occur at λ 5300 and λ 5800.

3 : 3 : 3′ : 3′-*Tetramethyl*-1 : 1′-*diethylindocarbocyanine Iodide.*—Trimethylindolenine ethiodide has been previously prepared by the action of methyl iodide on 2-methyl-1-ethylindole (König and Müller, *Ber.*, 1924, **57**, 144), but in the present work it was obtained by heating 2 : 3 : 3-trimethylindolenine (8·2 g.; 1 mol.) and ethyl iodide (5 c.c.; 1·2 mols.) in a sealed tube at 100° for 48 hours. After recrystallisation from rectified spirit, the ethiodide (yield, 61%) had m. p. 224° (decomp.) (Found: I, 40·2. Calc. for $C_{13}H_{18}NI$: I, 40·3%). The crude carbocyanine (yield, 86%), obtained by condensation with ethyl orthoformate, was recrystallised from dilute spirit acidified with hydrogen iodide, and was obtained in 75% yield. It forms pleochroic crystals, which are olive-green and steel-blue. If rapidly heated, it softens at 204—210°, or, if slowly heated, melts and resolidifies; it melts at 260—263° (decomp.) (Found: I, 24·8. $C_{27}H_{32}N_2I$ requires I, 24·8%). In spirit solution, the chief absorption maximum occurs at λ 5480 and there is a weaker band with its maximum at λ 5120. When added to the emulsion, the dye shows moderate sensitising action and has three maxima, at λ 5350, 5750 and 6000, respectively. In sensitising by bathing, it shows two maxima, at λ 5320 and λ 5700, and its action is more powerful.

RESEARCH LABORATORY,
ILFORD, LIMITED, ILFORD, E.

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CCCLXXV.—*Quaternary Salts in the Benzselenazole Series.*

By Leslie Marshall Clark.

The zinc salt of *o*-aminoselenophenol, which reacts with benzoyl chloride to give phenylbenzselenazole (Bauer, *Ber.*, 1913, **46**, 92), reacts similarly with formic acid to give *benzselenazole* (I).

(I.) $C_6H_4<^{Se}_{N}>CH$ $\qquad$ $\left[C_6H_4<^{Se}_{NMe\cdot CHO}\right]_2$ (II.)

Benzselenazole methiodide, when titrated in aqueous solution with sodium hydroxide and phenolphthalein, requires two equivalents of alkali for neutralisation. The neutral solution reduces one equivalent of iodine, a compound, $(C_8H_8ONSe)_2$, being formed. This behaviour of benzselenazole methiodide is clearly analogous to that of benzthiazole methiodide (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353) and must be ascribed to formation of the carbinol base, subsequent opening of the heterocyclic ring to give the sodium salt of *o*-formylmethylaminoselenophenol, $CHO\cdot NMe\cdot C_6H_4\cdot SeNa$, and oxidation of this by iodine (or other mild oxidising agents) to *di*-o-*formylmethylaminodiphenyl diselenide* (II).

Similar reactions occur when 2-phenylbenzselenazole methiodide is treated with two equivalents of sodium hydroxide, followed by one of iodine, and are, therefore, probably general for all 2-alkyl- and 2-aryl-substituted benzselenazolinium salts.

Atmospheric oxidation of benzselenazole methiodide in ammoniacal solution gives *di*-o-*methylaminodiphenyl diselenide*, the formyl groups of (II) having been removed by contact with ammonium hydroxide. Similar treatment of benzthiazole methiodide gives di-*o*-formylmethylaminodiphenyl disulphide, di-*o*-methylaminodiphenyl disulphide being produced only when sodium hydroxide is substituted for ammonium hydroxide (compare Mills, Clark, and Aeschlimann, *loc. cit.*).

Confirmation of the correctness of the explanations advanced above is obtained by the benzoylation of the di-*o*-methylaminodiphenyl diselenide obtained from benzselenazole methiodide. The product is identical with the compound obtained from 2-phenylbenzselenazole methiodide by treatment with alkali and oxidation.

During the preparation of benzselenazole, *di*-o-*formylaminodiphenyl diselenide* was isolated as a by-product. This compound, when treated in alcoholic solution with stannous chloride, gave some benzselenazole by preliminary reduction to *o*-formylaminoselenophenol, which then underwent condensation by loss of water.

The formyl groups in di-*o*-formylaminodiphenyl diselenide are readily removed by heating with phenylhydrazine, since α-formylphenylhydrazine is obtained from the reaction mixture.

Experimental.

The zinc salt of *o*-aminoselenophenol was prepared by Bauer's method (*loc. cit.*), but a better yield (56%) of di-*o*-aminodiphenyl diselenide was obtained by oxidising the solution of *o*-aminoselenophenol, well stirred and cooled below 6°, with potassium ferricyanide instead of hydrogen peroxide.

Benzselenazole (I).—The zinc salt of *o*-aminoselenophenol (17 g.) was boiled during 14 hours with anhydrous formic acid (140 c.c.), and the solution poured into water; a light-coloured oil, which rapidly solidified, was then precipitated. Excess of ammonium hydroxide was added and the oily suspension and the solid deposit (A) were extracted by means of ether. The extract was dried over sodium carbonate, the solvent removed, and the residue distilled, giving *benzselenazole* (4·5 g.), a slightly yellow liquid, b. p. 154°/45 mm., having an odour very similar to that of benzthiazole (Found : N, 8·0. C_7H_5NSe requires N, 7·7%).

Benzselenazole Methiodide.—A mixture of the base (4·2 g.) and methyl iodide (5 g.) was kept for 24 hours and then heated on the water-bath for 3 hours. The resulting solid, after being washed with ether, crystallised from alcohol in very pale yellow needles (yield, 80%), m. p. 188—189° (Found : C, 29·4; H, 2·45; N, 4·2; I, 39·1; Se, 24·1. C_8H_8NISe requires C, 29·6; H, 2·5; N, 4·3; I, 39·2; Se, 24·4%). *Benzselenazole methopicrate*, obtained from the methiodide and picric acid in alcoholic solution, had m. p. 173° (Found : N, 12·8. $C_{14}H_{10}O_7N_4Se$ requires N, 13·2%).

Action of Sodium Hydroxide on Benzselenazole Methiodide.—Benzselenazole methiodide (1·500 g.) in aqueous solution required 9·3 c.c. of 1·02*N*-sodium hydroxide for neutralisation (Calc. for two equivs. of NaOH, 9·1 c.c.). On oxidation of the cold solution with potassium ferricyanide a yellowish, oily substance was precipitated. This was extracted with benzene, and the extract was dried over sodium carbonate and concentrated, and light petroleum added until a permanent turbidity appeared; *di-o-formylmethylaminodiphenyl diselenide* (II) slowly separated in small, colourless prisms, m. p. 104° (Found : C, 45·0; H, 3·8; N, 6·7; *M*, cryoscopic in camphor, 424. $C_{16}H_{16}O_2N_2Se_2$ requires C, 45·1; H, 3·75; N, 6·6%; *M*, 426).

Oxidation of o-Formylmethylaminoselenophenol by Iodine.—Benzselenazole methiodide (0·3240 g.), dissolved in water, was treated with two equivalents of sodium hydroxide. The slightly yellow solution required 9·3 c.c. of *N*/10-iodine for oxidation (Calc. for 1 equiv.,

10·0 c.c.). The error in the titration is undoubtedly due to atmospheric oxidation, which appears to be more rapid in the case of the selenophenols than in that of the thiophenols. Di-*o*-formylmethylaminodiphenyl diselenide, m. p. 104°, was isolated as before.

Atmospheric Oxidation of o-Formylmethylaminoselenophenol.—Benzselenazole methiodide (0·3 g.) was dissolved in water (30 c.c.), and ammonium hydroxide (2 c.c.; *d*, 0·880) added. The solution became yellow and slightly turbid; after it had been kept for several hours in the dark, a crystalline, yellow substance separated on the surface. If the concentration of ammonium hydroxide was greater than that stated, the crystals were accompanied by a yellow oil. When the solution had lost its yellow colour, the crystals were removed and purified by evaporation of a solution in light petroleum. After several repetitions of this procedure, *di-o-methylaminodiphenyl diselenide* was obtained, m. p. 89° (Found: C, 45·3; H, 4·2; N, 7·5. $C_{14}H_{16}N_2Se_2$ requires C, 45·4; H, 4·3; N, 7·6%). This diselenide is very readily soluble in organic solvents. It separates from ether in yellow, hexagonal tablets, very similar in appearance to those of di-*o*-methylaminodiphenyl disulphide (Mills, Clark, and Aeschlimann, *loc. cit.*).

Di-*o*-methylaminodiphenyl diselenide (0·2 g.), shaken with benzoyl chloride and sodium hydroxide, gave a pasty mass; after crystallisation from aqueous alcohol, this had m. p. 170°, alone or when mixed with di-*o*-benzoylmethylaminodiphenyl diselenide obtained from 1-phenylbenzselenazole methiodide (see below).

1-*Phenylbenzselenazole Methiodide.*—1-Phenylbenzselenazole (2 g.), prepared by Bogert and Chen's method (*J. Amer. Chem. Soc.*, 1922, **44**, 2355), was heated at 100° during 26 hours with methyl iodide (2·5 c.c.). After removal of the excess of methyl halide, the residue was extracted with ether to remove unchanged base. The crude *methiodide* crystallised from alcohol in golden-yellow needles, m. p. 211—212° (decomp.) (Found: I, 31·5. $C_{14}H_{12}NISe$ requires I, 31·75%). 1-*Phenylbenzselenazole chloroplatinate* was prepared from alcoholic-hydrochloric acid solutions of the base and platinic chloride and separated in flattened, yellowish-brown needles [Found: Pt, 20·8. $(C_{13}H_9NSe)_2H_2PtCl_6$ requires Pt, 21·0%].

Action of Sodium Hydroxide on 1-*Phenylbenzselenazole Methiodide: Di-o-benzoylmethylaminodiphenyl Diselenide.*—The methiodide (0·210 g.), dissolved in water, was titrated at 50° with sodium hydroxide and phenolphthalein. The addition of each portion of alkali caused the transient red coloration of the indicator which is characteristic of pseudo-base formation (Required: 19·3 c.c. of *N*/20-sodium hydroxide. Calc. for two equivs., 19·5 c.c.). This solution, cooled and titrated with 0·0625*N*-iodine, required 7·0 c.c. for complete

oxidation, whereas the amount calculated for one equivalent of iodine is 8·4 c.c. This discrepancy must again be ascribed to atmospheric oxidation. The colourless solid, *di-o-benzoylmethylaminodiphenyl diselenide*, which separated after the iodine oxidation crystallised from aqueous alcohol in stout needles, m. p. 170° (Found : C, 58·4; H, 4·1; N, 5·1; Se, 27·0. $C_{28}H_{24}O_2N_2Se_2$ requires C, 58·1; H, 4·15; N, 4·8; Se, 27·3%).

Di-o-formylaminodiphenyl Diselenide.—The deposit A, obtained from the formylation of *o*-aminoselenophenol, crystallised from alcohol (charcoal) in soft, pale yellow needles, m. p. 174°. Analysis showed it to be *di-o-formylaminodiphenyl diselenide*, which must have been produced by atmospheric oxidation of aminoselenophenol to the corresponding diselenide, followed by formylation of the amino-groups (Found : C, 42·4; H, 3·1; N, 7·0. $C_{14}H_{12}O_2N_2Se_2$ requires C, 42·2; H, 3·0; N, 7·0%).

Preparation of Benzselenazole from Di-o-formylaminodiphenyl Diselenide.—The diselenide (1·8 g.), dissolved in alcohol–acetone, was reduced with excess of stannous chloride in dilute hydrochloric acid solution. The mixture was heated at 100° for ½ hour and then evaporated to dryness. The residue was treated with sodium hydroxide solution and the oil liberated was taken up in ether, dried over sodium carbonate, and distilled in a vacuum. The distillate was heated with excess of methyl iodide at 70—80° for 4 hours, the uncombined methyl iodide boiled off, and the partly crystalline residue dissolved in acetone; on addition of ether to this solution a crystalline deposit was formed which, after purification, melted at 187°, alone or when mixed with authentic benzselenazole methiodide.

Reaction between o-Diformylaminodiphenyl Diselenide and Phenylhydrazine.—The diselenide (0·5 g.) was heated with phenylhydrazine (1·2 g.) at 100° for 3 hours and the orange-red oil produced was cooled and diluted with ether; colourless plates of α-formylphenylhydrazine were deposited; these, after crystallisation from water, had m. p. 144°, alone or when mixed with an authentic specimen.

A satisfactory method for the estimation of selenium in organic compounds of the type described in this paper is as follows : The compound is decomposed by treatment with 50 c.c. of 8% potassium permanganate solution and 10 c.c. of concentrated nitric acid. The mixture is evaporated to dryness on the steam-bath, 10 c.c. of the permanganate solution and 5 c.c. of nitric acid are added to the residue, and the evaporation is repeated. The addition of permanganate and acid and the evaporation are repeated, 80 c.c. of concentrated hydrochloric acid are added to the residue, and the

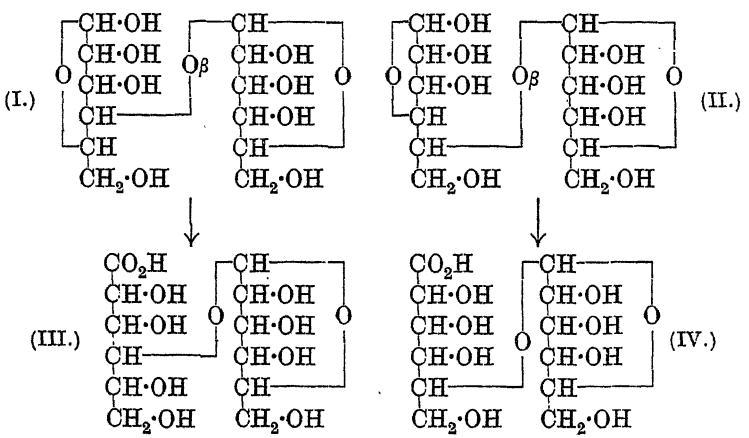
mixture is boiled until chlorine and nitric acid are removed. The solution is then diluted and selenium determined by reduction with sulphurous acid.

22 STANLEY ROAD, TEDDINGTON. [*Received, October 6th*, 1927.]

CCCLXXVI.—*The Constitution of the Disaccharides. Part XVI. Cellobiose.*

By WALTER NORMAN HAWORTH, CHARLES WILLIAM LONG, and JOHN HERBERT GEOFFREY PLANT.

A CONSTITUTIONAL study of cellobiose was undertaken in this series (Part V) six years ago (Haworth and Hirst, J., 1921, **119**, 193), and the experimental results were as follows: Methylated cellobiose ⟶ crystalline tetramethyl glucose + crystalline 2 : 3 : 6-trimethyl glucose; and a structural formula was ascribed to the disaccharide on this basis. In common with all carbohydrate formulæ, this constitution was modified by the recognition of the revised formula of glucose in its normal derivatives (Charlton, Haworth, and Peat, J., 1926, 98), and the structure represented by (I) was assigned to cellobiose by the latter authors:

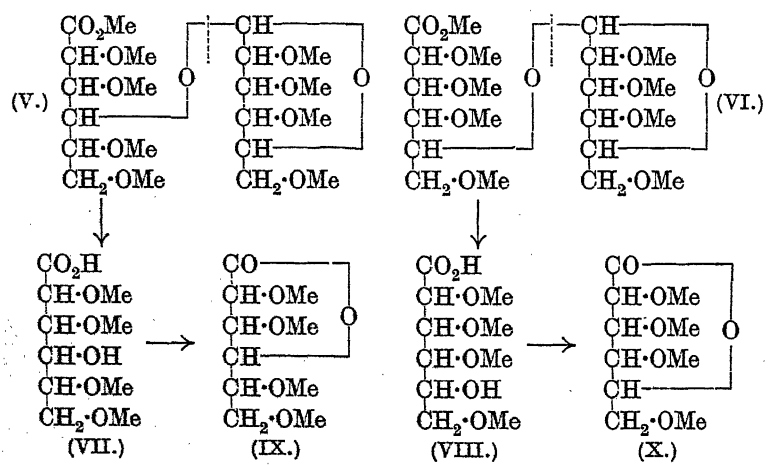


Consideration was given to an alternative formula for cellobiose (II), and it was stated that the isolation of 2 : 3 : 6-trimethyl glucose by cleavage of methylated cellobiose rendered it possible to regard the attachment of the reducing hexose component through position (5) to the other hexose residue, in which case the oxide ring of this first residue would be a butylene or γ-oxide (1 : 4) and not an amylene or δ-oxide (1 : 5). In the former case, cellobiose would be

to the extent of one residue a γ-sugar, but this was stated to be an unlikely contingency. Whilst making this reservation, therefore, the formula (I) for cellobiose was advocated, inasmuch as it correctly represented the properties of the disaccharide and was consistent with all the facts.

Meanwhile, we have instituted a series of experiments designed to eliminate any remaining doubt as to the structure of cellobiose. This disaccharide undergoes oxidation at its reducing position to give a monobasic acid designated cellobionic acid, and this compound can be formed only by opening of the ring of the reducing glucose component. The structure of cellobionic acid will thus be represented by formula (III) if (I) be accepted for the disaccharide, whilst (IV) will represent the acid if (II) be the structure of the disaccharide. It will therefore be seen that, in the two rival formulæ for the acid, the position of the oxygen link connecting the two C_6 chains differs in that in (III) this link engages the carbon in position (4), and in formula (IV) it engages the carbon in position (5).

We have been able to decide between these two alternative formulæ by methylating cellobionic acid completely, and the product, which was *methyl octamethylcellobionate*, was then submitted to hydrolysis. The cleavage products to be expected are seen to be different according as we accept formula (V) or formula (VI) as a correct representation of the methyl octamethylcellobionate. In addition to 2 : 3 : 4 : 6-tetramethyl glucose, the cleavage products



should contain a monobasic acid of the C_6 series which, if formula (V) be correct, would be the γ-hydroxy-acid (VII); or if formula (VI)

be correct, the δ-hydroxy-acid (VIII). Since each of these acids is already known and has been fully characterised by one of us in earlier investigations, a way was opened up enabling us to reach a decision through identification of this essential product. It will be seen that an acid of formula (VII) would give on heating a 1 : 4- or γ-lactone, recognisable as 2 : 3 : 5 : 6-tetramethyl gluconolactone, and similarly an acid of formula (VIII) would yield a 1 : 5- or δ-lactone, identifiable as 2 : 3 : 4 : 6-tetramethyl gluconolactone; and since each of these lactones has been fully characterised and degraded by oxidation methods (Haworth, Hirst, and Miller, this vol., p. 2436), there can be no dubiety in assigning a final constitution to each of them, and therefore to cellobiose itself.

When methyl octamethylcellobionate was hydrolysed with mineral acid, the cleavage products were isolated in an analogous manner to that described in recent papers on maltose (Haworth and Peat, J., 1926, 3094) and lactose (Haworth and Long, this vol., p. 544). Crystalline 2 : 3 : 4 : 6-tetramethyl glucose was isolated (yield, 92·7% of the theoretical), and the acid product originally retained as the barium salt was regenerated and distilled as a lactone which crystallised, m. p. 26—27° (yield, 80% of the theoretical). This compound gave a phenylhydrazide of the corresponding acid, m. p. 135—136°, and the melting point was not depressed in admixture with the phenylhydrazide of 2 : 3 : 5 : 6-tetramethyl gluconic acid which had been prepared from (*a*) methyl octamethyl-maltobionate or methyl octamethyl-lactobionate or (*b*) 2 : 3 : 5 : 6-tetramethyl γ-glucose (1 : 4) (compare Haworth and Long, Haworth and Peat, *locc. cit.*).

Again, the above lactone was shown to be identical with 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone isolated from the sources (*a*) and (*b*). There was, therefore, no doubt that the tetramethyl gluconic acid which had been formed from methyl octamethylcellobionate was that represented by formula (VII), since the lactone referred to is indicated by formula (IX). The results furnish evidence which seems to us conclusive in favour of the formulation (V) for methyl octamethylcellobionate, and therefore, if this be accepted, and it be assumed that no displacement of the biose linking had occurred in any of these transformations, cellobionic acid should be expressed by formula (III) and cellobiose by (I). This experimental result substantiates the constitutional formula which had previously been advocated by one of us and serves to remove the need for any reservation in favour of formula (II).

It should be noted in this connexion that, as indicated by Haworth and Peat (*loc. cit.*), maltose possesses the same structural formula as

cellobiose, the essential difference between these two bioses being that maltose is a glucose-α-glucoside and cellobiose a glucose-β-glucoside.

These experimental results are opposed to the views of Irvine (*Chemical Reviews*, 1927, **4**, 216), who has perceived a difference in the positions of (*a*) the biose linking in maltose and cellobiose and (*b*) the oxide ring in each of these bioses (compare Irvine and Black, J., 1926, 869; Irvine and Macdonald, *ibid.*, 1508; Irvine and Robertson, *ibid.*, 1496).

EXPERIMENTAL.

Cellobiose octa-acetate (m. p. 223—225°), prepared as described by Haworth and Hirst (J., 1921, **119**, 193) from pure cellulose, was hydrolysed by alcoholic potash to give potassium cellobiosate, and a representative sample of the latter was converted into cellobiose having $[\alpha]_D$ +24° ($c = 3{\cdot}33$) (equilibrium value) (Maquenne, *Bull. Soc. chim.*, 1904, **31**, 854). The remaining portion of potassium cellobiosate was dissolved in a little water, and bromine was admitted, which speedily dissolved. The solution was kept in a stoppered bottle at room temperature for 10 days; it was then almost devoid of reducing action towards Fehling's solution. The unchanged bromine was removed by aeration, followed by treatment with hydrogen sulphide. The colourless solution was shaken with finely ground litharge, filtered, then agitated in presence of silver oxide in the dark, and filtered. Hydrogen sulphide was again passed into the solution, and the excess of this gas removed by aeration. The clear solution was warmed gently for a day in presence of calcium carbonate, filtered, and evaporated to small bulk. This contained calcium cellobionate along with potassium bromide.

Methyl Octamethylcellobionate.—The methylation of calcium cellobionate was carried out in a similar manner to that described in the case of the corresponding salt of maltobionic acid (Haworth and Peat, *loc. cit.*), methyl sulphate and sodium hydroxide being used initially, followed by several treatments with moist silver oxide and methyl iodide, and finally by dry silver oxide and methyl iodide. The crude product at this stage was a yellow, mobile liquid (7·1 g.; OMe, 54·6%). This distilled under 0·05 mm. from a bath heated to 203°, and the first fraction (1·5 g.) of low boiling point was rejected. The major portion of the distillate (5·1 g.) was a pale yellow, viscid syrup, $n_D^{13°}$ 1·4604 (Found: OMe, 54·3%). The latter was again distilled under 0·05 mm., the first fraction (0·3 g.) being collected on heating the bath to 176°, and the main fraction (4·6 g.) distilled at 169—171°/0·05 mm. from a bath heated

to 192°. This product did not reduce Fehling's solution and had $n_D^{14°}$ 1·4609, and the analytical data agreed with the formula of *methyl octamethylcellobionate* (Found: C, 52·0; H, 8·3; OMe, 54·3. $C_{21}H_{40}O_{12}$ requires C, 52·1; H, 8·3; OMe, 57·6%).

Hydrolysis. The above product (3·1 g.) was dissolved in 100 c.c. of 7% hydrochloric acid, and heated at 80—90° until the specific rotation of the solution appeared to show no further changes. $[\alpha]_D^{19°}$ + 5·4° (initial), + 32·1° (after 1 hour), 50·2° (2 hours), 54·6° (3 hours), 55·0° (4 hours; constant). At this stage finely divided barium carbonate was gradually added, and the solution aerated at 50° to assist the neutralisation. After being kept over-night, the solution was filtered and evaporated at 40°/16 mm. To the white residue, alcohol was added and distilled off under 16 mm. The dry solid was digested with boiling ether many times and the collected extracts were evaporated, leaving a syrup which crystallised in colourless needles. These were purified from light petroleum (weight, 1·5 g.; yield, 92·7%) and identified as 2 : 3 : 4 : 6-tetramethyl glucose by the following properties: m. p. 93—94°; mixed m. p. determination with a specimen prepared from methylated maltose, 93—94°; $[\alpha]_D^{14°}$ in water (c = 2·02) + 99·9° (5 mins.), 88·0° (30 mins.), 85·5° (1 hour), 83·0° (2 hours; constant).

The original white residue of barium salts from which the tetramethyl glucose had been extracted was warmed to eliminate traces of ether, dissolved in water, and treated with a slight deficiency of dilute hydrochloric acid. The water was evaporated at 50°/15 mm. and finally the residue was heated at 60—80°/0·09 mm. for 2 hours. Repeated digestion of this dried residue with boiling ether yielded 1·2 g. (80% of the theoretical) of a pale yellow syrup which distilled under 0·09 mm. from a bath heated to 119°, leaving only 0·1 g. of residue.

Nucleation of the cooled distillate with 2 : 3 : 5 : 6-tetramethyl gluconolactone (from methyl octamethyl-lactobionate; Haworth and Long, this vol., p. 547) resulted in immediate crystallisation; m. p. 26—27°, mixed m. p. determination 26—27° (with the specimen from which the nucleus had been taken) (Found: C, 51·2; H, 7·8; OMe, 51·4. Calc.: C, 51·3; H, 7·7; OMe, 53·0%).

Phenylhydrazide of 2 : 3 : 5 : 6-*Tetramethyl Gluconic Acid.*—A specimen of the above lactone (0·16 g.) in contact with phenylhydrazine (1 mol.) dissolved in ether was heated on a water-bath. Crystals of the phenylhydrazide separated, m. p 135—136° (from benzene), mixed m. p. 135—136° [with specimens prepared from the 2 : 3 : 5 : 6-tetramethyl gluconolactone obtained from methyl octamethylmaltobionate (Haworth and Peat, *loc. cit.*) and from 2 : 3 : 5 : 6-tetramethyl (γ-)glucose (Charlton, Haworth, and Peat, *loc. cit.*)]

(Found : C, 56·1; H, 7·65; OMe, 35·0; N, 8·45. Calc. : C, 56·1; H, 7·6; OMe, 36·3; N, 8·2%).

The authors are indebted to the Department of Scientific and Industrial Research for grants to two of them.

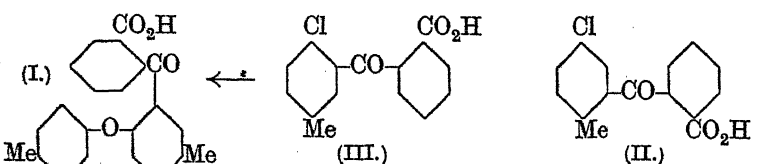
UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, October 13th*, 1927.]

CCCLXXVII.—*Substituted Diaryl Ethers. Part II. The Friedel–Crafts Reaction applied to Di-*p*-tolyl Ether.*

By JOSEPH REILLY and PETER J. DRUMM.

ALTHOUGH there are two similar benzene nuclei in di-*p*-tolyl ether in both of which substitution may occur, the authors find that this ether yields only monoketonic derivatives in the Friedel–Crafts reaction. The condensation of di-*p*-tolyl ether proceeds more readily with phthalic anhydride than with benzoyl chloride, substitution occurring in one position only; from benzoyl chloride more than one substance appears to be formed.

Condensation of 2-hydroxy-5-methylbenzophenone-2′-carboxylic acid with *p*-bromotoluene gives 2-o-*carboxybenzoyldi*-p-*tolyl ether* (I), identical with the product of interaction between phthalic anhydride and di-*p*-tolyl ether. The formation of a 2-ketone in the latter reaction is what would be expected and is in line with the authors' recent work on the nitration of di-*p*-tolyl ether (this vol., p. 68) showing that the oxygen atom exerts the main orienting influence.



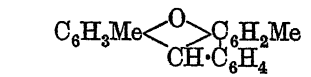
The substance (I) has also been obtained by condensing *p*-cresol with the chloromethylbenzophenone-*o*-carboxylic acid which Heller and Schulke (*Ber.*, 1908, **41**, 3627) prepared from *p*-chlorotoluene and phthalic anhydride. Their ketone therefore has formula (III), not (II), the chlorine atom exerting a greater directive influence than the methyl group.

The product obtained by heating (I) with concentrated sulphuric acid is, not an anthraquinone derivative, but 2 : 7-dimethylfluoran,

identical with that obtained by Drewsen (*Annalen*, 1882, **212**, 341) from phthalic anhydride, *p*-cresol, and sulphuric acid; it gives 2 : 2′-dihydroxy-5 : 5′-dimethylbenzophenone and benzoic acid on fusion with potassium hydroxide.

Although 2-*benzoyldi*-p-*tolyl ether* (formula as I) has not been directly synthesised, its constitution as an ortho-substituted diaryl ether is indicated by the following facts. Its solutions in acetic and sulphuric acids are yellow and fluorescent, indicating xanthhydrol formation through ring closure. From these solutions, 9-phenyl-2 : 7-dimethylxanthen was isolated identical with that obtained by Feuerstein and Lipp (*Ber.*, 1902, **35**, 3255) by the dry distillation of 6 : 6′-dihydroxy-3 : 3′-dimethyltriphenylmethane.

The conditions employed by Feuerstein and Lipp in preparing the phenyldimethylxanthen were so drastic that its constitution is not beyond doubt. Moreover, its formation from benzoyldi-*p*-tolyl ether in acetic acid—the change is more readily effected by boiling alcoholic hydrochloric acid—is difficult to understand. It seems to the authors that the substance may be a fluorene,



but to this view there is the objection that the molecule of such a substance would be in a state of considerable strain; the formula also shows linkage at a position (1 in the xanthen ring) which is not only sterically hindered but is also meta with respect to the oxygen atom. In support of the fluorene formula, however, may be quoted the following facts: (1) Phenyldi-α-naphthylcarbinol, on boiling with acetic acid, changes into phenyldi-α-naphthafluorene (Schoepfle, *J. Amer. Chem. Soc.*, 1922, **44**, 190); (2) Ullmann and Mourawiew-Winigradoff (*Ber.*, 1905, **38**, 2213), on heating diphenyl-α-naphthylcarbinol with an acetic acid solution of sulphuric acid, zinc chloride, or hydrochloric acid, obtained phenylchrysofluorene. In offering the above suggestion, it is appreciated that phenyl groups exhibit less tendency than naphthyl groups to formation of fluorene linkages.

It was not found possible to prepare the oxime from 2-*o*-carboxybenzoyldi-*p*-tolyl ether (I), and the phenylhydrazone was only obtained under drastic conditions. These appear to be cases of steric hindrance by substituents in the two ortho-positions with respect to the carbonyl group. 2-Benzoyldi-*p*-tolyl ether, under identical conditions, did not give a phenylhydrazone, the reaction proceeding in a different direction.

Contrary to the generally accepted view that the reaction between benzoyl chloride and phenols in presence of aluminium chloride

results in poor yields of hydroxybenzophenones unless the hydroxyl group has been previously protected (compare Fries and Finck, *Ber.*, 1908, **41**, 4276; Heller, *Ber.*, 1913, **46**, 1498), it is now found that with acetylene tetrachloride as solvent 2-hydroxy-5-methylbenzophenone is obtained in good yield from *p*-cresol and benzoyl chloride.

EXPERIMENTAL.

2-o-*Carboxybenzoyldi*-p-*tolyl Ether* (I).—A mixture of di-*p*-tolyl ether (8 g.) and phthalic anhydride (6 g.) was slowly added to anhydrous aluminium chloride (9 g.), covered with dry carbon disulphide and protected from moisture. After 12 hours, the product was poured on ice, the carbon disulphide and other volatile products were removed in steam, and the colourless residue was repeatedly dissolved in aqueous sodium hydroxide and precipitated by dilute acid. The product then crystallised from aqueous ethyl alcohol in long, hexagonal prisms (yield, 70%), m. p. 155° (Found: C, 76·2; H, 5·5; *M*, cryoscopic in naphthalene, 360. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%; *M*, 346).

Repetition of the above experiment, twice the quantities of phthalic anhydride and aluminium chloride being used, gave the same product, namely, 2-o-*carboxybenzoyldi*-p-*tolyl ether*, in approximately the same yield, no diketonic derivative being isolated.

Synthesis of 2-o-*Carboxybenzoyldi*-p-*tolyl Ether*.—*p*-Bromotoluene (10 g.), the dipotassium derivative (10 g.; dried at 120° in a vacuum) of 2-hydroxy-5-methylbenzophenone-2′-carboxylic acid prepared by Ullmann's method (*Ber.*, 1919, **52**, 2102), and a trace of copper bronze (Naturkupfer C, washed with ether to remove oily impurities) were heated in absolute-alcoholic solution in a sealed tube for 10 hours at 200°. The product was distilled in steam; unchanged *p*-bromotoluene passed over, followed by di-*p*-tolyl ether (1 g.). The residual oil was extracted with hot dilute sodium hydroxide solution, the extract acidified, and the viscous precipitate obtained crystallised from acetic acid (80%); 2-o-carboxybenzoyldi-*p*-tolyl ether slowly separated in colourless prisms, m. p. 154—155°, identical with the ether described above.

2-o-Carboxybenzoyldi-*p*-tolyl ether is readily soluble in glacial acetic acid, absolute alcohol or ether and very sparingly soluble in light petroleum (b. p. 60—80°) or water. It dissolves in concentrated sulphuric acid to an orange solution exhibiting a greenish fluorescence; the colour is discharged on dilution with water. Its *silver* salt is sparingly soluble in water, but readily soluble in dilute aqueous ammonia (Found: Ag, 23·9. $C_{22}H_{17}O_4Ag$ requires Ag, 23·8%). The ether, on fusion with potassium hydroxide, is decom-

posed into di-*p*-tolyl ether and phthalic acid. It unites with anhydrous aluminium chloride to give an orange-coloured solid.

The formation of di-*p*-tolyl ether in the above reaction was at first suspected to result from hydrolysis of the 2-*o*-carboxybenzoyldi-*p*-tolyl ether formed, but on heating *p*-bromotoluene and alcoholic potassium hydroxide under identical conditions di-*p*-tolyl ether was isolated in small quantity.

2-*o*-Carboxybenzoyldi-*p*-tolyl ether was recovered unchanged after being heated with hydroxylamine hydrochloride in strongly alkaline solution for 8 hours on the water-bath. The *phenylhydrazone* was obtained only by heating the ether (1 mol.) and phenylhydrazine (2 mols.) for 3 hours at 160—170°. The cooled product was extracted with very dilute hydrochloric acid; from an alcoholic solution of the residue, the *phenylhydrazone* separated in pale yellow needles, m. p. 156° (Found: N, 6·6. $C_{28}H_{24}O_3N_2$ requires N, 6·4%).

Action of Sulphuric Acid on 2-o-*Carboxybenzoyldi*-p-*tolyl Ether.*—The ether (1 g.) and concentrated sulphuric acid (8 c.c.) were heated on a boiling water-bath for 3 hours. The solution was then cooled and mixed with ice, and the precipitate obtained was collected and digested with aqueous sodium hydroxide solution; the extract was purple, owing probably to the presence of an anthraquinone derivative. The part insoluble in alkali was crystallised from absolute ethyl alcohol, 2 : 7-dimethylfluoran being obtained in colourless, glistening prisms (yield, 90%), m. p. 254° (Drewsen, *loc. cit.*, gives m. p. 246°) (Found: C, 80·6; H, 5·1. Calc. for $C_{22}H_{16}O_3$: C, 80·5; H, 4·9%).

The nature of this substance was established by fusion with potassium hydroxide at 220—240°. The dark yellow aqueous extract of the product was acidified and then boiled with sufficient alcohol to give a clear solution; on standing, yellow needles of 2 : 2′-dihydroxy-5 : 5′-dimethylbenzophenone separated which, after one recrystallisation from alcohol, had m. p. 104—106°. Distillation in steam of the filtrate from the fusion product gave benzoic acid.

Equal weights of 2-*o*-carboxybenzoyldi-*p*-tolyl ether and phosphorus pentachloride were heated in benzene solution until evolution of hydrogen chloride ceased. To the cooled, light orange solution was added the same weight of anhydrous aluminium chloride; hydrogen chloride was then again evolved. The deep red solution was finally refluxed for a short time and poured on ice; the product, isolated in the usual way, was 2 : 7-dimethylfluoran.

Constitution of Heller and Schulke's Ketone (III).—A mixture of the potassium salt of Heller and Schulke's ketone (*loc. cit.*) (1 mol.),

potassium *p*-tolyloxide (1·5 mols.), *p*-cresol (solvent), and a trace of copper bronze was slowly heated, with stirring, to 200°; at 160° potassium chloride separated. After being heated for an hour at 190—200°, the product was dissolved in water, and the solution was extracted with ether, acidified, and extracted with chloroform. The chloroform was evaporated, and the residue dissolved in hot acetic acid (80%); 2-*o*-carboxybenzoyldi-*p*-tolyl ether slowly crystallised in short, colourless prisms, m. p. 153—154°.

2-*Benzoyldi*-p-*tolyl Ether* (formula as I).—The preparation from di-*p*-tolyl ether (7 g.), benzoyl chloride (5 g.), and aluminium chloride (12 g.) is very similar to that of the carboxylic acid (I) described above. The residue obtained after the steam-distillation set to a crystalline mass which separated from boiling, absolute ethyl alcohol in colourless, glistening rhombohedra (5·5 g.), m. p. 185—186° (Found: C, 83·1; H, 6·3. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). A viscous oil (4 g.) obtained from the mother-liquor resisted all attempts to crystallise it.

A second experiment with di-*p*-tolyl ether (7 g.), benzoyl chloride (10 g.), and aluminium chloride (24 g.) was carried out under identical conditions, but the same monobenzoyl compound was obtained (7·8 g.) and no dibenzoyl compound was isolated.

2-*Benzoyldi*-p-*tolyl ether* is readily soluble in chloroform, acetone or benzene, much less soluble in ethyl alcohol, and insoluble in light petroleum (b. p. 60—80°). It dissolves in concentrated sulphuric acid to a bright yellow solution with a green fluorescence; dilution with water discharges the fluorescence but not the colour. It combines with anhydrous aluminium chloride to form a bright orange solid which immediately decomposes in contact with water.

Glacial acetic acid in contact with 2-benzoyldi-*p*-tolyl ether is coloured yellow; it becomes orange on heating and reddish-orange on boiling. On cooling, 9-phenyl-2 : 7-dimethylxanthen separates in colourless, glistening needles which, alone or mixed with an authentic specimen, melt at 195—196° (Found: by the micro-method, C, 87·8; H, 6·2; *M*, cryoscopic in camphor, 312. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%; *M*, 286. Calc. for $C_{21}H_{16}O$: C, 88·7; H, 5·6%; *M*, 284). The same xanthen was obtained when 2-benzoyldi-*p*-tolyl ether was heated with phenylhydrazine at 160° for 2 hours.

2-*Hydroxy*-5-*methylbenzophenone*.—To *p*-cresol (10 g.) and benzoyl chloride (14·1 g.), dissolved in dry acetylene tetrachloride and protected from moisture, anhydrous aluminium chloride (26·7 g.) was added during 1 hour. The mixture was then heated for 4 hours at 100—110°, hydrogen chloride being copiously evolved. After cooling, the dark brown solution was poured into water, a dark oil

separating. On distillation in steam, acetylene tetrachloride passed over, followed slowly by a light yellow oil which quickly solidified and was highly pure 2-hydroxy-5-methylbenzophenone (yield, 80%), m. p. 84·5° (Cox, *J. Amer. Chem. Soc.*, 1927, **49**, 1029, gives m. p. 87°).

2-p-*Tolyloxy*-5-*methylacetophenone*, prepared in the usual manner, was obtained as a red oil which was purified by distillation; the fraction, b. p. 320—340°, set to a crystalline solid which separated from alcohol in colourless, glistening plates, m. p. 168° (Found: C, 79·6; H, 7·0; *M*, cryoscopic in naphthalene, 251. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%; *M*, 240). This ketone has the characteristic odour of acetophenone and is readily soluble in ether, benzene, or hot alcohol. It dissolves in sulphuric acid to a yellow solution.

Addendum.—Since the above work was completed, a paper by Rosenmund and Schulz has appeared (*Arch. Pharm.*, 1927, **265**, 308), in which it is stated that the reaction between phenols and acid chlorides with aluminium chloride in nitrobenzene solution, giving phenolic ketones, is of general applicability. The unique behaviour of nitrobenzene is ascribed to its solvent action on the aluminium chloride complexes. Monohydric phenols react readily except when the *p*-position to the hydroxyl group is occupied. We have observed that acetylene tetrachloride also can be used as solvent in the preparation of phenolic ketones, and this holds even when the *p*-position to the hydroxyl group is occupied (*e.g.*, the yield of 2-hydroxy-5-methylbenzophenone is 80%).

UNIVERSITY COLLEGE, CORK. [*Received, September 5th*, 1927.]

CCCLXXVIII.—*The Action of Alkalis on Clay.*

By HENRY BOWEN OAKLEY.

IN the study of the physical and chemical properties of soils, much attention has always been directed towards the clay fraction which, together with humus, is responsible for the colloidal properties of the soil, and is one of the most reactive components chemically.

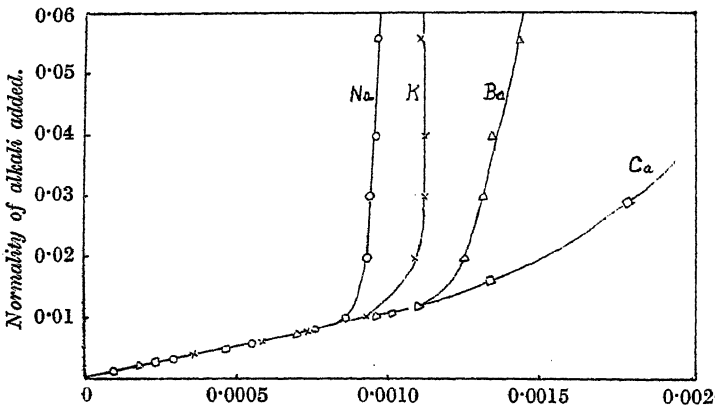
Although many diverse hypotheses have been put forward to account for the " absorption " of bases by clay, the trend of modern opinion is to regard the action as chemical in nature, being due to the formation of insoluble aluminosilicates, as opposed to the hypothesis of " physical absorption of ions," which is still largely adopted in many branches of colloid chemistry. The view that clay acts as a weak acid towards alkalis is supported by the electrometric titration curves of Bradfield (*J. Amer. Chem. Soc.*, 1923,

45, 2669), and is confirmed by the results presented in this paper. A fairly full bibliography on this subject is given by Bradfield (*J. Amer. Soc. Agronomy*, 1925, **17**, 253).

The clays used in this work were separated by sedimentation in 0·05% sodium carbonate, flocculated by dilute hydrochloric acid (N/100), and purified to a high resistance by dialysis (Joseph and Hancock, J., 1924, **125**, 1888).

The Effect of the Concentration of Alkali on the Amount of Base removed from Solution by Clay.—The clay used in these experiments was No. 10195 prepared from a heavy cotton soil: it was practically identical with No. 6640 (Joseph and Hancock, *loc. cit.*). 10 C.c. samples of a 5% suspension were treated with different

FIG. 1.



Equivalents of base taken up by 1 *g. of clay in the presence of* N/2*-chloride;* 1 % *suspensions.*

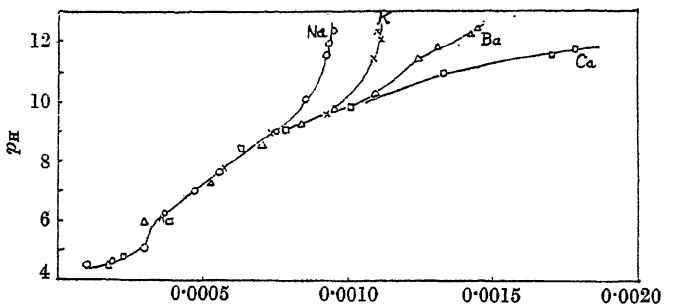
quantities of standard alkali in centrifuge tubes. Water and a standard chloride solution of the appropriate base were added to make the total volume 50 c.c. and N/2 with respect to the chloride. This treatment completely flocculated the clay. The tubes were centrifuged, and 25 c.c. of the clear, supernatant liquid were treated with excess of N/10-hydrochloric acid and titrated back with N/10-sodium hydroxide, as this procedure was found to give the sharpest end-point. Methyl-orange was used as indicator. A further portion was withdrawn for the p_H determination in a Clark cell with a Leeds and Northrup potentiometer. From the change in concentration of the alkali, the amount removed by the clay can be calculated, since any soluble silicates or aluminates which may be formed behave in titration as free alkali.

The results are illustrated in Figs. 1 and 2. The equivalents of base taken up per g. of clay are identical for sodium, potassium,

barium, and calcium up to an initial concentration of alkali of 0·01*N*, or an equilibrium p_H of about 9; but with a further increase in the concentration of alkali the amounts taken up are in the increasing order sodium, potassium, barium, and calcium. The amounts of sodium and potassium taken up attain fairly constant values above a p_H of 11, whereas barium and calcium show no such limit. This order is the same as that found for amorphous silica (Joseph and Oakley, J., 1925, **127**, 2813), and suggests that the quantity of any base retained in the solid phase is partly determined by the solubility or stability of the aluminosilicates and their products of decomposition with increasing concentrations of alkali.

The Total Amounts of Sodium and Calcium Hydroxides neutralised by Clay.—That the quantity of bases removed in the solid phase

FIG. 2.



Equivalents of base taken up by 1 g. of clay in the presence of N/2-chloride; 1% suspensions.

is closely connected with the solubility of the products of combination is illustrated by the following results for calcium and sodium hydroxides, giving the total amount of alkali neutralised in the two cases. No chloride was added in this experiment, and a lower concentration of clay was used so that the necessarily dilute calcium hydroxide could be present in a greater excess than in the previous experiment.

To determine the total sodium hydroxide neutralised, a series of p_H measurements was made on caustic soda solutions of various strengths; the hydroxyl-ion concentrations were then calculated by subtracting these values of the p_H from the values of Michaelis for $\log 1/K_w$ at the appropriate temperature (Clark, "The Determination of Hydrogen Ions," p. 29). These calculated values of the hydroxyl-ion concentrations were then plotted against the concentration of sodium hydroxide. In a similar manner, the concentration of hydroxyl-ions was calculated from the p_H of the clay suspensions. The corresponding concentration of sodium

hydroxide was read from the curve, and this value was subtracted from the original concentration of caustic soda added. The temperatures varied from 30° to 35°, but this was allowed for both in the calculation of the p_H and in the subsequent calculation. The error in the determination of the total hydroxide neutralised may be as much as 10%. An exactly similar method was applied for calcium. The results are in the following table (compare Bradfield, *Soil Sci.*, 1924, **17**, 411).

Total amount of calcium and sodium hydroxide neutralised by clay after standing 1 day. Concentration: 0·52% clay.

Initial conc. of hydroxide.	Equiv. of alkali neutralised per g. of clay.		Final p_H.	
	Sodium.	Calcium.	Sodium.	Calcium.
0·036	0·0018	0·0027	11·92	11·81
0·020	0·0012	0·0021	11·67	11·50
0·008	0·0010	0·0012	11·00	10·75

These results show that, although the total sodium hydroxide neutralised is about twice the amount taken up in the solid phase (compare Fig. 1), thus demonstrating the formation of soluble compounds, yet the amount of calcium hydroxide neutralised is still greater, although no soluble compounds are formed. This is shown by the fact that, for an initial calcium hydroxide concentration of 0·038 and a final p_H of 11·93, the amount of calcium hydroxide neutralised per g. of clay, as calculated from the p_H, was 0·0031, whereas that calculated from titration of the excess of alkali was 0·0032. (The concentration of the clay was 0·26%.)

The compounds formed by silica and calcium hydroxide were also found to be insoluble, but in this case they were equivalent in amount to the total sodium compounds formed under the same conditions (Joseph and Oakley, *loc. cit.*).

The influence of the concentration of the sodium on the amount of base taken up by 1 g. of clay is illustrated by the following figures with various concentrations of chloride:

Conc. of NaOH, 0·04*N*; conc. of clay, 1%.

Conc. of NaCl	1·0	0·5	0·2	0·1
Na taken up (equiv. × 10^4) ...	9·68	9·56	9·17	9·15
p_H	12·10	12·16	12·22	12·25

A comparison of the effect of *N*-solutions of chlorides on the amounts of sodium, potassium, and calcium taken up by 1 g. of clay is given in the following figures (equivs. × 10^4):

Chloride.	Concentration of hydroxide.		
	0·08*N*-NaOH.	0·08*N*-KOH.	0·03*N*-$Ca(OH)_2$.
0·0*N*	8·46	10·4	14·9
1·0*N*	9·60	12·8	17·8

As had been previously found with silica, the addition of the chloride of the base to an alkaline suspension always increased the amount of base taken up.

The removal of the base from solution by clay is very rapid. This is illustrated by the following figures for 1 g. of clay.

Conc. of NaOH, 0·04*N*; conc. of NaCl, 0·5*N*; conc. of clay, 1%.

Time	10 mins.	1 hr.	3 hrs.	1 day
Na taken up	9·7	9·9	9·8	10·3

The Relation between the Soluble and Insoluble Sodium Compounds with Clay.—In order to determine the relation between the soluble and the insoluble sodium compounds formed with increasing concentrations of sodium hydroxide, a series of 0·5-g. samples of clay was treated with different concentrations of standard caustic soda, the volume being always 50 c.c. After standing for 1 hour, 10 c.c. were withdrawn for a p_H determination. The remainder was filtered through a collodion filter and an aliquot portion of the clear filtrate was titrated with standard acid and alkali as before. The difference between the total amount neutralised (calculated from p_H) and the amount taken up (calculated from the titration) gave the equivalents of sodium neutralised in a soluble form. These results are in the following table.

The amounts of sodium neutralised in the solid phase and in solution by 1 g. of clay after 1 hour. Concentration of clay, 1%.

Initial conc. of NaOH.	p_H at equilibrium.	Equivs. Na in solid phase, × 10^4.	Equivs. Na neutralised in solution, × 10^4.	Ratio, Soluble/ Insoluble.
0·07	12·33	9·7	7	0·72
0·04	12·03	9·7	5	0·51
0·02	11·60	9·9	2	0·20
0·01	10·72	8·1	1	0·11
0·006	9·77	5·4	0·6	0·11
0·004	8·62	3·9	0·1	0·02

The amount of soluble sodium compounds formed is small until the p_H exceeds 10·5, or until the concentration of alkali is greater than 0·01*N*.* This is just the concentration at which the amounts of different bases taken up begin to diverge (Fig. 1). These results leave no doubt, I think, that the later process of the neutralisation of bases by clay at higher concentrations of hydroxide differs from the initial reaction at low concentrations, in that the more concentrated alkali begins to break down the clay substance, forming

* In the case of silica, the amount of sodium in the solid phase is always very small compared with the total silicate formed (J., 1925, **127**, 2816, Table IV).

silicates and aluminates. In the case of calcium, these are insoluble, and in the case of sodium, they are easily soluble, whilst potassium and barium occupy intermediate positions. In one special experiment, the amount of lithium taken up by 1 g. of clay in the presence of 0·5*N*-lithium chloride was $9{\cdot}0 \times 10^{-4}$ equiv. at a p_H of 9·8, and the amount for sodium under similar conditions was $9{\cdot}5 \times 10^{-4}$.

At the lower concentrations of alkali (below 0·01*N*), the identity of the amounts of different bases taken up shows that these solubility relationships do not come into play, the compounds formed with any of the bases being equally insoluble. In this case, there appears to exist a direct reversible equilibrium between these insoluble compounds and the bases in solution, the equilibrium with alkalis having characteristics similar to those of a weak acid in true solution; this is indicated by the shape of the curves for sodium in Figs. 2 and 4.

From these curves it is seen that the clay acid is half converted into its sodium compound at about p_H 8. If the laws of dissociation of a weak acid are applicable, this would mean that its dissociation constant is about 10^{-8}. Bradfield (*J. Physical Chem.*, 1924, **28**, 170), from the variation of the p_H with concentration of a clay suspension, calculated a value of 3×10^{-7}.

Further evidence that clay behaves as an insoluble acid in direct equilibrium with the bases in solution is afforded by the liberation of acid when a neutral salt is added to clay, and by the fact that clay so treated hydrolyses on being washed with water, giving an alkaline solution. The equivalence of the exchange of bases when clay is washed with the salt of another base also supports the view that the reactions are purely chemical in nature (*Trans. Faraday Soc.*, 1925, **22**, 251). The speed with which all these reactions take place and the influence of various electrolytes on the electrokinetic potential and stability of clay suspensions (Oakley, *J. Physical Chem.*, 1926, **30**, 902) seem to indicate that the reactions are mainly ionic. The fact that clay, with its weakly acidic properties, can remove some of the base from the salt of a strong acid, thus setting free this acid, also receives a natural explanation on the above view.

In order to determine the composition of the material dissolved from the clay, 5 g. of clay were shaken with *N*/10-sodium hydroxide in the presence of *N*/2-sodium chloride, the volume being adjusted so that the concentration of the clay was 1%. This was centrifuged and the clear supernatant liquid analysed for silica, alumina, and ferric oxide. This treatment was repeated four times for increasing periods of time with fresh additions of sodium hydroxide and chloride. Two further experiments were made with two separate

portions of the stock clay for periods of 1 hour and 3 days, respectively. The results are in the following table.

Material dissolved from 1 g. of clay by $N/10$-sodium hydroxide in the presence of $N/2$-sodium chloride. Concentration of clay (No. 14637), 1%.

A. Successive treatments on the same portion of clay.

Time.	SiO_2.	$Al_2O_3 + Fe_2O_3$.	$SiO_2/(Al_2O_3 + Fe_2O_3)$.
5 mins.	0·0050	0·0046	1·1
1 hour	0·0052	0·0020	2·6
1 day	0·0107	0·0018	6·0
3 days	0·0109	0·0017	6·4

B. Treatment on two separate portions of clay.

1 hour	0·0065	0·00466	1·41
3 days	0·0115	0·0044	2·62
Untreated clay	0·475	0·328	1·44

On the assumption that the soluble compounds formed are Na_2SiO_3 and $NaAlO_2$, the sodium so combined is $2·8 \times 10^{-4}$ and $4·4 \times 10^{-4}$ equiv., respectively, for the last two experiments (the ferric oxide also was estimated in these cases). The value obtained from p_H measurements after 3 days' standing was $4·5 \times 10^{-4}$, and the sodium removed in the solid phase was $7·6 \times 10^{-4}$. The figures in the last column show that the proportion of sesquioxides rapidly falls in successive treatments with caustic soda, there being a higher proportion of sesquioxides in the first extract than in the clay itself. Another notable result is that the amount of material dissolved increases very slowly on prolonging the time of contact of the alkali with the clay, and this independently of whether the clay has had previous treatments with caustic soda or not. These results suggest that the material which goes into solution strongly inhibits further solvent action of the alkali. Since the concentration of the sodium hydroxide is reduced only by about 15% in the case of the initial treatments, and by about 5% in the other cases, the decreased rate of solvent action is unlikely to be due to diminished alkali concentration.

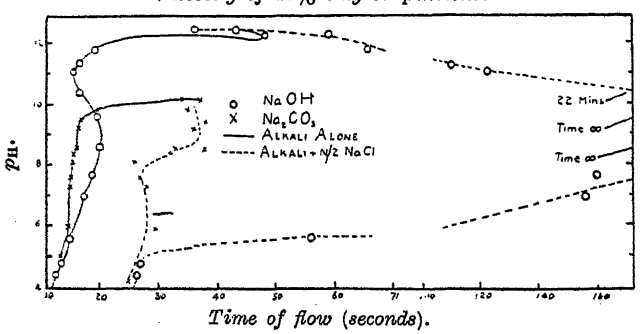
The Effect of Sodium Hydroxide and Sodium Carbonate on the Viscosity of Clay Suspensions.—It was thought that the difference in composition of the material removed by the early treatments compared with that from the later treatments might indicate that this material was identical with the hypothetical " layer of gel " on clay particles, which, according to some writers, gives clay its peculiar plastic and water-holding properties (*Brit. Assoc.*, 3rd Report on Colloid Chemistry, 1920, pp. 113—153).

If this is the case, the viscosity of clay in caustic soda solution of strength sufficient to dissolve this layer should be markedly less

than the value for clay in the presence of alkali too weak to dissolve the layer, since the particle size should be greatly reduced by the former treatment. Complicating factors in the comparison are the state of flocculation, and the state of saturation of the clay with regard to sodium. The times of flow of 10% suspensions of clay in an Ostwald viscometer were determined in a thermostat at 35°. One series of measurements was made on suspensions containing varying amounts of sodium hydroxide, and a similar series was made with sodium carbonate. After these measurements had been completed, sodium chloride was added in amount sufficient to make its concentration $N/2$. The times of flow of the deflocculated suspensions could be accurately repeated, but when the clay was flocculated, the time rapidly decreased with successive readings until an approximately constant value was reached, but this rose

FIG. 3.

Viscosity of 10% *clay suspensions.*



again on standing. The latter measurements are therefore very rough. The suspensions were too thick for the determination of their p_H; they were therefore diluted to one-fifth of their original concentration, and the p_H determinations were made on the diluted samples. If there was no buffer action, this dilution would decrease the p_H value by 0·7 unit, but since both the clay itself and the material dissolved by the alkali exert considerable buffer action, it is safe to conclude that the effect of dilution would not reduce the p_H by more than 0·3. The measurements were made on the suspensions after the addition of the sodium chloride.

The times of flow are plotted against the p_H in Fig. 3. The following data show the concentration of alkali added and the corresponding times of flow before the addition of sodium chloride. The time of flow of water was 10·4 seconds. [It is desirable to point out that the following figures cannot in any way be said to represent *true* viscosity values, for two reasons: (1) The rate of flow of the

uncoagulated suspensions was so high as to cause turbulent flow; and (2) Poiseuille's law is not obeyed by clay suspensions. Nevertheless, the results are of interest in showing that the comparative "thickness" of clay suspensions is affected differently by sodium hydroxide and by sodium carbonate.]

Conc. of NaOH or Na_2CO_3.	Time with NaOH (secs.).	Time with Na_2CO_3 (secs.).	Conc. of NaOH or Na_2CO_3.	Time with NaOH (secs.).	Time with Na_2CO_3 (secs.).
0·01	12·6	12·3	0·10	16·5	15·6
0·02	13·6	12·7	0·15	15·4	16·1
0·03	15·0	13·6	0·20	16·2	16·2
0·04	17·5	14·7	0·25	19·2	16·5
0·05	19·0	15·0	0·40	48·0	19·5
0·07	20·0	15·0	0·80	43·0	37·0
0·08	18·4	15·3			

The results show that at corresponding p_H values, the viscosity of clay treated with sodium carbonate is never greater than that of the clay treated with sodium hydroxide. The rapid rise in viscosity of the suspensions without sodium chloride at the highest values of the p_H is due to the flocculation of the clay by the alkali. Since the amount of material dissolved by the sodium hydroxide will be far greater than that dissolved by the sodium carbonate (carbonic acid being strong enough to decompose silicates and aluminates), it follows that this dissolved material cannot have existed in the clay in a particularly bulky and gelatinous condition. If this had been the case, its removal would have had a marked effect on the viscosity as compared with the values in the presence of sodium carbonate.

A striking feature of the results is that the curve for sodium hydroxide shows a maximum in viscosity between p_H 8 and 10, and this maximum is enormously enhanced when the clay is flocculated with sodium chloride. There is a complete absence of this effect with sodium carbonate, which suggests that it is connected with the much greater solvent power of the hydroxide. The hypothesis which accounts for the facts is that the sodium hydroxide at certain concentrations, instead of actually dissolving some of the clay, forms a comparatively non-viscous sol with this material. The addition of sodium chloride coagulates this sol, forming a coagulum of a very gelatinous nature. At higher concentrations of sodium hydroxide, this sol dissolves and cannot be coagulated by sodium chloride. This explains (1) why the maximum is only slight with caustic soda alone, but very pronounced in the presence of sodium chloride, (2) why the viscosity of the coagulated clay again falls when excess of caustic soda is added, and (3) why sodium carbonate does not show the effect.

This hypothesis is further supported by the fact that the clay

is more bulky with sodium hydroxide in the same range of p_H values at which the maximum in viscosity is observed, and that the maximum is not shown by sodium carbonate.

The following figures show the volume of 1 g. of clay (*i.e.*, of the clay plus its interstitial water after 10 minutes' centrifuging) after standing 1 day with various concentrations of alkali in the presence of *N*/2-sodium chloride.

Conc.	p_H with NaOH.	Vol., c.c.	p_H with Na_2CO_3.	Vol., c.c.	Conc.	p_H with NaOH.	Vol., c.c.	p_H with Na_2CO_3.	Vol., c.c.
0·0	4·0	4·1	—	—	0·1	12·3	5·1	8·3	4·1
0·02	7·6	4·6	—	—	0·2	12·9	4·7	8·8	4·3
0·03	8·0	5·4	—	—	0·3	13·1	4·4	9·0	4·2
0·04	9·5	5·7	—	—	0·5	13·3	4·2	10·2	4·3
0·05	11·1	5·5	8·1	4·0	1·0	13·6	4·1	10·4	4·5
0·07	12·2	5·3	—	—					

The fact that the clay without sodium hydroxide occupies the same volume as the clay in the presence of *N*-hydroxide affords further evidence that the material dissolved by the alkali is not specifically more bulky than the rest of the clay material.

Finally, the fact that the imbibitional water of the clay was unaltered by the prolonged treatment with sodium hydroxide points to the same conclusion. This water is the volume of water retained by 100 c.c. of the clay less the volume of xylene retained by the same clay after centrifuging for 40 minutes under a force of 1000 times gravity (compare Fisher, *J. Agric. Sci.*, 1924, **14**, 204). It was determined on the original clay (1) after drying with the addition of 9 c.c. of *N*/10-sodium hydroxide per g. of clay, and (2) on the clay left over after the four successive treatments with caustic soda described previously (p. 2825). This was washed until it was deflocculated and then collected on a collodion filter. Separate determinations were made, water and *N*-sodium chloride being used as the wetting liquids.

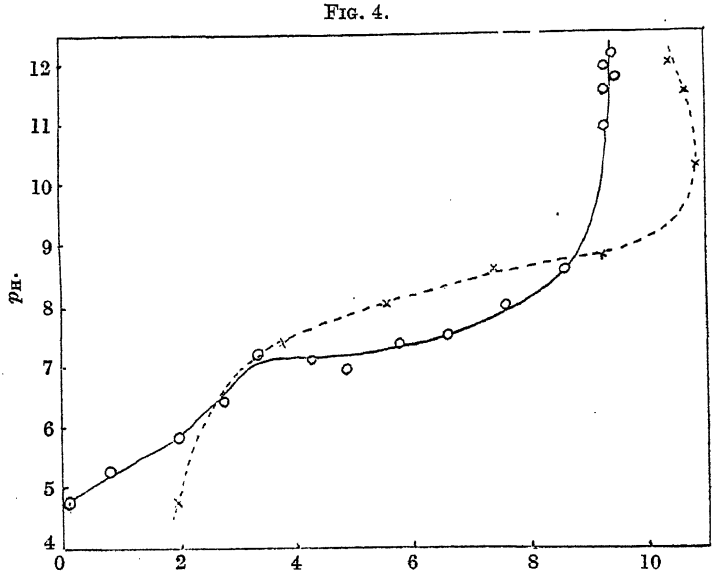
Imbibitional water of clay No. 14637.

	Water.	*N*-NaCl.
(1) 9×10^{-4} equiv. Na/g.	251	103
(2) Prolonged NaOH treatment	248	104

A Comparison of the Properties of a Synthetic Aluminosilicate and of Clays.—Although, in the comparison of different soil clays, some degree of correlation can be traced between base-absorbing capacity and certain colloidal properties such as heat of wetting, imbibitional water, and general clay-like properties, yet it is equally true that a substance having a composition similar to clay, a fair imbibitional water content, and a very large base-absorbing capacity may, nevertheless, show clay-like properties only to a very small

extent. This is well illustrated by the following experiments on a synthetic aluminosilicate. This was prepared (see de Sigmond, *Proc. 4th Inter. Confer. Pedology*, 1924, 2, 434) by mixing solutions of sodium aluminate and sodium silicate (both $N/10$ with regard to sodium; $Na_2O : SiO_2 = 1 : 2$) in such proportion that the molecular ratio $SiO_2 : Al_2O_3 = 3 : 1$. Under such conditions, as de Sigmond has shown (*loc. cit.*), almost complete precipitation takes place of the compound $3SiO_2,Al_2O_3,Na_2O,3H_2O$. When the p_H of the mixture was progressively altered by the addition of different

FIG. 4.



Equivalents of sodium taken up, $\times 10^4$.

Full curve: 1/2000 *mol.* (0·17 *g.*) *of synthetic aluminosilicate in* 50 c.c. *Dotted curve:* 1 *g. of clay No.* 14637; 1% *suspension.*

amounts of standard hydrochloric acid, the amount of sodium retained by the compound varied with the p_H in a manner rather similar to that in the case of clay (Fig. 4). This very highly gelatinous compound was washed several times by decantation after centrifuging, and evaporated to dryness on a water-bath with frequent stirring to cause the formation of small aggregates. It was then dried at 100° and subjected to a process of alternate grinding in a wet condition in an agate mortar and sedimentation. The product was kept for 4 weeks with $N/100$-hydrochloric acid, the acid being renewed at intervals. It was then washed by decantation and centrifuging until it deflocculated and the specific resistance of a 1% suspension was 13,000 ohms. The alternate

grinding and sedimentation was then repeated, but even after this, most of the material sedimented within 3 hours, so that it was still much coarser than clay, which may be stable for months. This material on standing developed an alkaline reaction (p_H 8). The following table compares the imbibitional water and the behaviour towards sodium and calcium hydroxides of this substance with the same properties of different clays and silica as given by Joseph (*J. Agric. Sci.*, 1927, **17**, 14).

Sample No.	Description.	Na taken up in solid phase: 0·5*N*-NaCl+ 0·04*N*-NaOH (1% clay).	Total NaOH neutralised (0·08*N*-NaOH; 1% clay).	Ca removed in solid phase (0·3% clay).	Imbibitional water.
14637	Gezira.	$10·0 \times 10^{-4}$	12×10^{-4}	30×10^{-4}	143
10118	Kaolin.	0·0	0·0	1	5
13107	Mongalla (red).	3·1	19	22	54
—	Bentonite.	7·6	20	36	362
—	Synthetic alumino-silicate.	24	40	51	74
—	Amorphous silica.	4	About 70	About 70	40
10120	Ball clay.	—	—	—	40

The synthetic product is remarkable for its high sodium-absorbing capacity. All the clays neutralise more calcium than sodium hydroxide. This may be connected with the fact mentioned by Vernadsky (*Rep. Brit. Assoc.*, 1923, 435) that it is a general property of zeolites to form additive compounds with calcium hydroxide. The synthetic material shows a marked contrast with kaolin both in its reactions with bases and in its imbibitional water. It retains 13% of moisture at 150°, in this respect also resembling clays. Kaolin has been prepared synthetically by Schwarz and Walcker (*Z. anorg. Chem.*, 1925, **145**, 304) by precipitating silicic acid with aluminium chloride in an *acid* medium.

Although the first-mentioned synthetic aluminosilicate resembled clay in some important respects, yet its physical properties, as exemplified by its plasticity in the hand, showed that this most characteristic property of clay was only present to a very limited extent—possibly this may be due to the coarseness of its particles. Notwithstanding that bentonite is by far the most highly colloidal clay-like substance known, yet it takes up less sodium than the Gezira clay, whilst silica, which has no clay-like properties, takes up more sodium than the Mongalla clay. The sodium absorption of these substances is therefore not necessarily related to their colloidal properties or to the fineness of division of their particles.

Summary.

1. Clay which has been purified after a mild acid treatment takes up equivalent quantities of bases up to a p_H of about 9.

When the p_H is greater than this, the amounts removed are in the order lithium < sodium < potassium < barium < calcium. These amounts are increased by the presence of neutral salts of the metals.

2. The amount of sodium hydroxide neutralised in the form of *soluble* compounds is negligible until the p_H is above 9, but increases rapidly when the alkalinity is greater than this.

3. These results, taken in conjunction with evidence from elsewhere, are accounted for on the supposition that clay is an insoluble or a colloidal weak acid in *direct* equilibrium with bases in solution, the salts formed with the various bases being equally insoluble; but unless the alkali is very dilute ($p_H = 9$), the clay begins to break down, giving silicates and aluminates. With sodium these are easily soluble, and with calcium they are insoluble, whilst barium and potassium occupy intermediate positions.

4. About 1% of the clay was immediately dissolved by $N/10$-sodium hydroxide, but this amount was only slightly increased on prolonged standing. Renewal of the alkali, however, rapidly caused the dissolution of 1% more. The ratio of silica to sesquioxides in solution increased from 1 to 6 in four successive treatments. The imbibitional water of the clay was unaltered by the above treatment.

5. The viscosity and specific volume of coagulated clay show pronounced maxima between p_H 8 and 10 with caustic soda, but not with sodium carbonate at the same p_H values.

6. In base-absorption, water-retention, and imbibitional water a synthetic aluminosilicate showed considerable analogy with clay, although the material was comparatively coarse and was only slightly "clay-like" to the touch. Large sodium absorption by aluminosilicates does not necessarily indicate highly developed colloidal properties or a particularly fine state of division. Comparisons are made between three different clays—kaolin, silica, and bentonite.

WELLCOME TROPICAL RESEARCH LABORATORIES,
KHARTOUM. [*Received, May 23rd*, 1927.]

CCCLXXIX.—*On Active Nitrogen. Part IV. The Independence of the Afterglow and the Chemical Properties of Active Nitrogen.*

By ERIC JOHN BAXTER WILLEY.

SINCE the discovery by the present Lord Rayleigh (Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 219) that nitrogen which has been subjected to the action of a condenser discharge at low pressures shows both

an afterglow and chemical activity, there has been much discussion as to whether this active modification of the element is (*a*) atomic, (*b*) molecular and metastable, or (*c*) triatomic. The evidence for each of these views may shortly be summarised:

(*a*) (i) The decay process of the glow follows a bimolecular law (Angerer, *Physikal. Z.*, 1921, **22**, 97).

(ii) An analysis of the banded afterglow spectrum (Birge, *Nature*, 1926, **117**, 80), critical potential measurements in connexion with this (Sponer, *Z. Physik*, 1925, **34**, 622), and observations upon the spectra excited by active nitrogen (Mulliken, *Physical Rev.*, 1924, **23**, 259, 767; 1925, **26**, 1) lead to the view that the energy associated with this glowing gas is of the order of 200,000—250,000 cals./g.-mol. (10—12 volts).

(*b*) Saha and Sur (*Phil. Mag.*, 1924, **118**, 421) consider that the spectroscopic evidence indicates a metastable molecule of heat of formation 190,000 cals./g.-mol.

(*c*) Trautz (*Z. Elektrochem.*, 1919, **25**, 299), from mathematical considerations, favours a triatomic molecule with a heat of formation of 5,000—10,000 cals./g.-mol.

The consensus of opinion regards active nitrogen as possessing a *high* heat of formation and its existence as due to atomic recombination, an excited or metastable and chemically reactive molecule thus being produced.

In Parts I, II, and III of this series (J., 1926, 1804; this vol., pp. 669, 2188), evidence has been presented for the view that the energy of active nitrogen is 45,000 cals./g.-mol. (2 volts), and deductions from the spectra excited by active nitrogen have been criticised on the ground that chemiluminescence has not been sufficiently considered as a possible means of production of these luminous phenomena (*Nature*, 1926, **118**, 735). Efforts recently made (Ruark, Foote, Rudnick, and Chenault, *J. Opt. Soc. Amer.*, 1927, **14**, 17) to answer these objections are unsatisfactory, since the calculations made here are based upon mercurous azoimide, HgN_3, and not upon the substituted ammonias, Hg_3N_2 and Hg_3N, which are the products of the reaction between active nitrogen and mercury vapour.

Thus we are left to reconcile two entirely different views on the energy and nature of active nitrogen, each supported by abundant experimental evidence, and as a tentative explanation it was suggested (Part II) that active nitrogen might emit its energy in a series of 45,000-cal. (2-volt) stages.

Early in 1925 it had been felt that certain seemingly inconsistent observations upon active nitrogen could best be explained by the theory that *two* luminous forms of the element were concerned,

differing both in chemical activity and in nature, but as this view led to the assumption of a possible change in the spectrum of the glow during decay, owing to the transformation rates of the two species not being the same, the hypothesis was for the time being abandoned. Dr. H. W. B. Skinner has recently suggested to the author that the discrepancy in these two sets of experiments can be overcome if we do not regard the chemically active nitrogen as luminous at all, but ascribe all the luminous phenomena (if this be possible upon the basis of available experimental evidence) to the effects of a few atoms produced at the same time as the former substance. This theory has, it is believed, been completely verified, for it has been found that the destruction of the glow by a second weak discharge and also by heat, noticed by Lord Rayleigh, is not accompanied by any decomposition of the chemically active nitrogen; furthermore, activity can be produced in the gas by the use of a discharge which does not give rise to any glow.

Experimental.

First Method.—Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1916, *A*, **92**, 438) that when a stream of glowing nitrogen is drawn through a second and weak discharge, the glow is completely or very largely destroyed, and it appeared possible that this second discharge might prove fatal to the luminous nitrogen without affecting the chemically active modification which is, *ex hypothesi*, also present. This possibility was tested in the following manner.

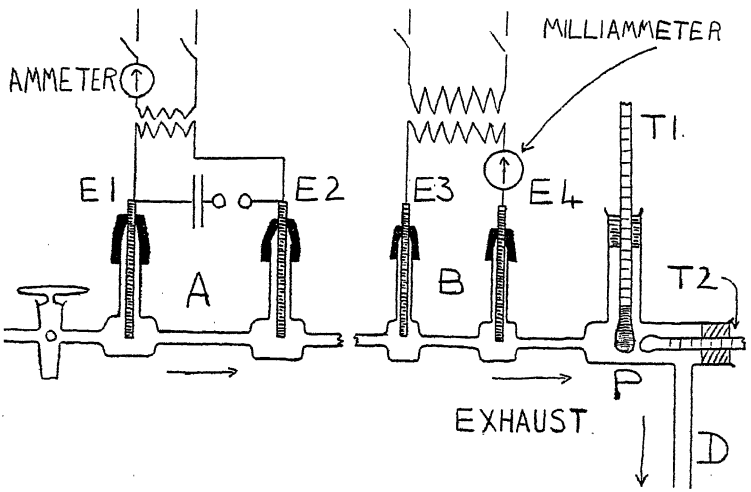
Nitrogen, purified as described in Part I, was drawn at 10 mm. pressure and a constant speed (1—3 litres/hr., at *N.T.P.*) through the discharge tubes A and B and the test chamber P to exhaust at D (Fig. 1). The aluminium electrodes E1, E2, E3, and E4 were held in position by rubber sleeves and their relative positions so adjusted that the distance between E2 and E3 was $1\frac{1}{2}$ times the distance between E3 and E4. Projecting into the test chamber P were two identical and carefully calibrated thermometers, T1 and T2, the bulb of the former being coated with a small and closely adherent piece of oxidised copper gauze, while the latter was bare. It was found in calibration experiments that, when active nitrogen was drawn through the apparatus, the glow was extinguished at the surface of the copper oxide, and that the rise in temperature shown by T1 above that indicated by T2 was strictly proportional to the concentration of active nitrogen at the position of the bulb of T1, this concentration being determined by means of nitric oxide, as described in Part I. This heating effect in T1 is obviously due to the catalytic decay of the active nitrogen at the copper oxide surface (compare Part III), as was proved by warming the tubes A and B

by small flames while a stream of inert nitrogen was drawn through the apparatus; the temperatures recorded on T1 and T2 were then identical.

The difference in temperature between T1 and T2 is thus a measure of the concentration of active nitrogen in the gas. A strong discharge, capable of developing the afterglow, was maintained in A from the coil, condensers, and spark gaps connected as shown, and a weak direct induction coil or transformer discharge from another circuit could, if desired, be run in B.

Lord Rayleigh's observation as to the destruction of the afterglow in these circumstances was confirmed, no luminosity being visible in the gases emerging from B when a weak discharge was maintained

FIG. 1.



between E3 and E4. (Any tendency for the auxiliary discharge to wander and pass between E2 and E3, E2 being connected to earth, was overcome by the electrode-spacing arrangement already mentioned.)

It was found, however, that provided too strong a discharge was not employed in B, the concentration of active nitrogen as measured on T1 and T2 did not change appreciably, in spite of the complete destruction of the glow by the auxiliary discharge; too strong a discharge in B destroyed both the glow and the chemical activity (Table I). The conditions necessary for the retention of the latter were best realised in practice by means of a discharge from a small transformer run off the 100-volt A.C. mains and provided with a series resistance of 825 ohms in the primary; the secondary current was then about 0·1 milliamp. (R.M.S. value) at 500 volts. The same

TABLE I.

No.	No. of observ-ations.	T1.	T2.	T1—T2.	Flow speed of gas at 13 mm. press. (c.c./hr.).	Auxiliary trans-former discharge.	Effect on afterglow.
1	9	1·6°	1·2°	0·4°	—	Coil.	Completely extinguished.
2	8	1·0	1·0	0·0	—	Weak.	,, ,,
3	15	1·0	1·0	0·0	—	,,	,, ,,
4	11	0·9	0·9	0·0	—	,,	,, ,,
5	17	2·7	1·3	1·4	2800	Medium.	,, ,,
6	8	4·3	0·6	3·7	3000	Strong.	,, ,,
7	10	2·9	0·4	2·5	—	,,	,, ,,
8	10	0·8	0·6	0·2	1900	Weak.	,, ,,
9	12	2·0	0·8	1·2	2000	,,	,, ,,
10	12	2·1	0·7	1·4	,,	Medium.	,, ,,
11	12	2·1	0·6	1·5	,,	,,	,, ,,

effect could be produced by the use of a direct coil discharge in B, but on account of the difficulty in regulation, the transformer was more generally used.

Furthermore, whilst in some cases a decrease in the concentration of active nitrogen was noticed, this was by no means comparable with the complete or almost complete destruction of the afterglow, and hence it appears that there is no simple relation between the intensity of the afterglow and the amount of chemically active nitrogen present.

Second Method.—In view of the comparatively insensitive nature of this device for detecting and determining the active nitrogen, the experiments were repeated, the estimations being carried out with nitric oxide; the other experimental arrangements remained unaltered. The technique of this method has been considerably improved and a short account of it may be given.

The nitrogen from the discharge tube B entered the reaction chamber at E (Fig. 2), and at N an inlet was provided for the nitric oxide, regulation of this gas being effected by means of the capillary choke at C and the tap S5. (The nitric oxide was prepared by dropping a solution of sodium nitrite into an acidified solution of ferrous sulphate, and was dried by phosphorus pentoxide.) The gases then passed to exhaust *via* the two-way tap S1, the condensing trap R1, and the second two-way tap S2. The system S3, R2, and S4 was identical with and parallel to the circuit just described. One side of S1 and S3 was connected to a supply of pure, dry hydrogen, and S2 and S4 were connected to exhaust and also to a train of absorption bulbs for the determination of the nitrogen peroxide. Hence, by the use of these two condensing systems, continuous estimations of the concentration of active nitrogen can be made without stopping the apparatus; the nitrogen peroxide

produced by the action of the active nitrogen upon nitric oxide condenses in R1 (or R2), which is cooled by liquid air. At the end of the experiment the gas stream is diverted to the other condensing system, the contents of R1 are allowed to warm to room temperature, and then blown by means of hydrogen (admitted at S1) through a train of absorption bottles containing a 10% solution of potassium iodide, the current of gas being maintained for some 20 minutes in order to clear the last traces of nitric oxide from the solution; the iodine is then titrated by means of standard sodium thiosulphate solution and the concentration of active nitrogen

FIG. 2.

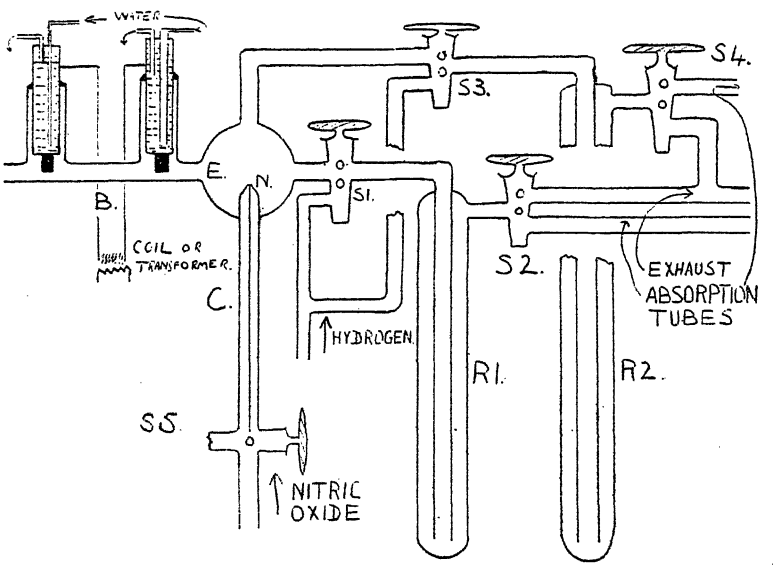


TABLE II.

Series.	No. of expts.	% Active nitrogen. (1) main discharge.	(2) main + auxiliary discharge.	Difference (2) − (1).	Auxiliary transformer discharge.
1	5	0·90	1·20	0·30	Weak.
2	4	2·30	2·50	0·20	,,
3	4	1·70	1·70	0·00	,,
4	4	1·75	2·00	0·25	,,
5	5	1·40	1·30	−0·10	Strong.
6	7	1·85	1·75	−0·10	,,
7	5	1·15	1·30	0·15	Weak.
8	8	1·30	1·30	0·00	,,

calculated as already described (Part I). The results of these experiments are given in Table II, and it will be noticed that, whilst in some cases the concentration of active nitrogen has diminished,

yet in other cases it has increased when the second discharge is employed. Since in every case the destruction of the glow is complete in the gases issuing from the auxiliary discharge, it appears that the results already obtained are confirmed, and that it is possible by this method to destroy the glow and yet retain the chemical properties of active nitrogen.

Third Method.—It was felt that these observations could be made still more convincing if a stream of non-luminous but chemically active nitrogen could be obtained by a single operation, and in view of the known production of active nitrogen in the arc, where none of the luminous phenomena connected with active nitrogen are to be seen (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 260), it was decided to study the effect of the uncondensed discharge upon nitrogen.

For this purpose, the apparatus employed was as in Fig. 2, except that the tubes A and B were replaced by another discharge tube with water-cooled Armco electrodes. The discharge was obtained from a rotary converter and transformers and took 10—20 milliamps. at 2000—3000 volts; in these circumstances, the emergent gases showed no perceptible luminosity but contained a considerable quantity of active nitrogen (Table III). No traces appeared here

TABLE III.

Series	1	2	3	4	5	6	7
No. of expts.	6	6	4	6	5	3	5
% Active nitrogen	0·84	0·98	1·28	0·64	0·85	1·52	1·52

of the green flame usually to be seen where nitric oxide enters a stream of glowing nitrogen, and hence we must conclude that most probably this particular development of luminosity is independent of the actual chemical reaction in progress (compare Lord Rayleigh, *Proc. Roy. Soc.*, 1911, *A*, **86**, 56). Furthermore, strong indications of the presence of active nitrogen were obtained by the use of the two-thermometer device already described.

Fourth Method.—The methods of extinguishing the luminosity of the active nitrogen have hitherto been electrical in nature, and it is obviously of importance that other means should be attempted in order that a satisfactory mechanism may be formulated for the glow-destruction process. Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) that, when a stream of glowing nitrogen is drawn through a tube which is heated, the luminosity ceases at the hot portions and reappears in the colder parts if the temperature is not too high; if the tube be heated too strongly, however, the glow is not restored at all, and it was thought advisable to study this phenomenon in the light of the present observations.

The apparatus employed is as in Fig. 2, except that the auxiliary discharge tube was replaced by a U-tube of some 10″ over-all length and ¼″ internal diameter; determination of the active nitrogen was made with nitric oxide as before. The U-tube was immersed in an electrically heated bath of heavy paraffin; for temperatures above 250° the paraffin was replaced by a mixture of sodium and potassium nitrates.

When a stream of glowing nitrogen was drawn through the apparatus at a rate of 2000 c.c./hr. and 10 mm. pressure, the luminosity was considerably enhanced as the temperature of the bath was raised from 20° to 80°; from this point to about 225° no appreciable change in intensity was noticed, but at 235° the luminosity began to decrease in the gas entering the detection chamber, at 250° the effect was pronounced, and at 300—320° the gas lost all glow. Contrary to the observations of Lord Rayleigh, the glow did not as a rule reappear beyond the hot zone when once it had been destroyed, although a 2-litre chamber was provided in the exhaust line in order that this point might be examined; in some cases, however, his observations were confirmed, and it appears that the nature of the hot surface is a very important factor in this connexion.

TABLE IV.

Series.	No. of expts.	Temp. of bath.	Glow.	% Active nitrogen.
1	2	15°	Strong.	0·64
	2	80	Slightly enhanced.	0·73
	1	139	" "	0·64
	1	257	" "	0·66
	1	252	" "	0·69
2	3	15	Strong.	0·71
	3	330	Practically extinguished.	0·71

Determinations of the active nitrogen in these experiments showed (Table IV) that, in spite of the alterations in the degree of luminosity, the concentration of the active gas remained sensibly unchanged throughout.

Discussion.

The experiments just described provide, it is thought, not only a fairly complete solution to the difficulty in reconciling spectroscopic and other optical work upon active nitrogen with the observations made upon the same subject in this laboratory, but also an explanation of certain phenomena alluded to by Lord Rayleigh and others.

Just before these experiments were completed, Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536) showed that the concentration of active nitrogen (measured chemically) and the intensity of the glow are not simply related to one another, at least four

terms being necessary in any expression connecting these two quantities. Details of their experimental procedure are not available, but the present work is in complete agreement with theirs. It may also be noticed that Koenig and Elöd (*Ber.*, 1914, **47**, 516) suspected that the presence of a glow was not a necessary criterion of chemical activity in nitrogen, but here again no experimental evidence was adduced. Furthermore, Lord Rayleigh has stated that "there does not appear to be any close or necessary connexion between the luminous phenomena associated with active nitrogen and the chemical ones" (J., 1918, **113**, 200; see also *Proc. Roy. Soc.*, 1913, *A*, **88**, 539). It appears that we must decide between two theories for an explanation of these phenomena:

(i) Active nitrogen may be regarded as a homogeneous substance which emits its energy in two or more stages, one of these being invariable and giving rise to the chemical activity, and the other or others being capable of modification so that the residual energy may be lost either as ultra-violet radiation or by an increase in the kinetic energy of the molecule. Saha and Sur (*loc. cit.*) regard the visible or α-radiation of the afterglow as *secondary* (the primary band in nitrogen lying in the vicinity of $\lambda = 1400$ Å.U.); it is possible therefore that some influence might lead to suppression of these α-bands and a corresponding development of other parts of the spectrum without affecting the chemical activity.

(ii) The whole of the observations and measurements which have been made with regard to active nitrogen can, in the author's opinion, be much more readily explained if it is assumed that the luminous and chemically active forms are quite distinct, although usually coexistent. The multiplicity of ionised and excited bodies produced by the discharge in any gas renders this quite likely, and examples are known of the formation under these conditions of more than one active form of an element, *e.g.*, the active oxygen, distinct from ozone, of Koenig and Elöd (*loc. cit.*), and the mono-, di-, and tri-atomic forms of hydrogen, all chemically active, whose existence has been claimed severally by Bonhoeffer (*Z. physikal. Chem.*, 1924, **113**, 199; 1925, **116**, 114, 391; 1926, **119**, 474; *Z. Elektrochem.*, 1925, **31**, 521), Phipps and Taylor (*Physical Rev.*, 1927, **29**, 309), and Wendt and Landauer (*J. Amer. Chem. Soc.*, 1922, **44**, 510).*

* It may be suggested that differences in the reactions of active hydrogen reported by certain of these investigators, *e.g.*, the formation of ammonia with nitrogen, noticed by Wendt and Landauer (*loc. cit.*) and denied by Bonhoeffer (*loc. cit.*; see also Paneth, Klener, and Peters, *Z. Elektrochem.*, 1927, **33**, 102), may be due to differences in their experimental conditions leading to the formation of different substances: the chemical activity of H, H_2, and H_3 is not likely to be the same.

If this view is adopted, it is apparent that the difficulties discussed earlier are overcome, since the observations of an active nitrogen made by spectroscopists and by workers in this laboratory have really been upon different modifications of the same element. The author now suggests that active nitrogen consists of a mixture of (i) metastable molecules with a heat of formation of *ca.* 45,000 cals./g.-mol. (2 volts), which are exclusively responsible for the chemical activity, and (ii) a much smaller proportion (probably of the order of 10^{-7}) of atoms which upon recombination produce high-level excited molecules, the energy set free, equivalent to 200,000—250,000 cals./g.-mol. (10—12 volts) being liberated as radiation; all the luminous phenomena and excitation of spectra, with the possible exception of certain cases of chemiluminescence arising from reactions of the 2-volt metastable molecules, are to be ascribed to this second constituent.

The decay of the afterglow follows a process which is bimolecular only with respect to the atoms, but is in reality a ternary reaction, for it has been shown (Herzfeld, *Z. Physik*, 1922, **8**, 132; Polyani, *ibid.*, 1920, **1**, 337; Born and Franck, *Ann. Physik*, 1925, **76**, 255) that, when two atoms recombine to form a diatomic molecule, the presence of a third body is nearly always necessary in order that considerations of the conservation of energy and momentum shall be satisfied. Such a view would presuppose a relation between the total pressure of the gas and the rate of decay of the afterglow; this has actually been observed by Lord Rayleigh (*Proc. Roy. Soc.*, 1916, *A*, **92**, 438) and studied by the present author, and it is hoped to publish details in a later communication.

The action of traces of impurities in developing the afterglow would appear to be adequately accounted for by Lord Rayleigh's original explanation (*Proc. Roy. Soc.*, 1912, *A*, **86**, 262; **87**, 179). Its behaviour towards heat and cold will be discussed in a later communication.

The catalytic destruction of the glow by surfaces, and by copper and other metals in particular, may readily be explained by the well-known analogous case of the surface recombination of hydrogen atoms. The extinction of the luminosity when a metal surface begins to be active in promoting the decay of the *chemically* active nitrogen is also accounted for when we remember that the surface is, *ex hypothesi*, composed of the metal, and not of the nitride, when the point of activity is reached; there is no apparent reason why a nitride surface should catalyse the recombination of nitrogen atoms, but the parent metal itself may, from the analogy already mentioned, be very effective in this connexion. It follows that the action of the discharge in extinguishing the luminosity is not intrinsically

electrical, but that the bombardment of the glass of the discharge tube by the ions and electrons present simply leads to the production of a " clean " surface, upon which the recombination of atoms can take place with ease; heat also leads to the production of this very active surface. The production of a few ions during the decay of the afterglow in phenomena studied by Constantinides (*Physical Rev.*, 1927, **30**, 95) is probably due to a side reaction among the atoms undergoing recombination on the surface.

It is clear that the relationship between concentration of active nitrogen, C, and glow intensity, I, as well as the magnitude and sign of dI/dC at any instant, will vary with the nature and area of the surfaces present. It appears probable that the mechanism whereby the chemically active nitrogen is destroyed in the discharge is analogous to that of the electrical production of ozone, and that the same complicated mixture of electrical and surface factors is involved: much more experimental evidence is needed upon this point.

It remains to discuss the probable nature of the chemically active modification of nitrogen. If this were triatomic, it would be expected that such a large molecule should condense easily (see Lord Rayleigh, *Proc. Roy. Soc.*, 1911, *A*, **86**, 56), and the author is indebted to Sir J. J. Thomson for the information that evidence is not lacking that such a separation can be effected under appropriate conditions.

The present author suggests, however, that the most cogent evidence as to the nature of active nitrogen is provided by the compounds it produces in its chemical reactions. With the metals, compounds are produced which, as a rule, give quantitative yields of ammonia when hydrolysed, *e.g.*, magnesium nitride; pentane gives hydrogen cyanide, amylenes, and ammonia (Koenig and Elöd, *loc. cit.*); and in general *when active nitrogen reacts with other substances it gives rise to derivatives of ammonia and not to substituted azoimides, hydrazines, etc.* These substances are invariably of the type produced in the few reactions of *inert* nitrogen, and hence the presumption is that active and ordinary nitrogen cannot be very different in structure. It is clear that if active nitrogen were atomic in character we should have to postulate dissociation of the molecule as an invariable prelude to the reactions of *inert* nitrogen, which does not appear likely. May it not be that the active modification is simply an isomeride of nitrogen, such as an acetylenic molecule? By analogy with its family congeners of the Periodic Table, nitrogen might be expected to exhibit allotropy, but much more experimental evidence is necessary before any conclusions can be reached upon this point.

Summary.

Four series of experiments are described in which it is shown that nitrogen can be chemically active and yet show no visible luminosity whatever. These are believed to indicate that "active" nitrogen consists of a mixture of a non-luminous, chemically active substance together with a very small proportion of atoms, the latter being responsible, upon a termolecular recombination, for the afterglow and the greater part of the excitation of spectra observed when various substances are admitted to the glowing gas. The heats of formation of the two varieties, the former of which is regarded as being most probably a metastable diatomic or an acetylenic molecule, are respectively about 45,000 and 200,000—250,000 cals./g.-mol.

This explanation is thought to reconcile the chemical and spectroscopic views, and also accounts for the whole of the phenomena connected with active nitrogen.

The author's thanks are due to the Department of Scientific and Industrial Research for a grant which enabled the converter and transformers to be purchased; to Dr. E. K. Rideal for his continued interest in these researches; to Mr. R. E. D. Clark, who has proved a capable assistant in some of the experimental work; and above all to Dr. H. W. B. Skinner, to whom this particular investigation must be dedicated.

Addendum.—Since the above was written, Crew and Hulbert (*Physical Rev.*, 1927, **30**, 124) have described some experiments on the dissociation of gases in the discharge at low pressures (5 mm. and less). The extent of dissociation is about 100% for wet hydrogen, rather less for the dry gas, 60% for oxygen, but close to zero for nitrogen, carbon monoxide, and carbon dioxide under the same conditions; the results with uncondensed and with condensed discharges, the latter producing the afterglow in nitrogen, are almost identical. This would appear to show once again that the chemically active nitrogen (which is produced to the extent of at least 5% under these conditions) cannot be atomic in character, and the work confirms the author's view upon this subject.

LABORATORY OF PHYSICAL CHEMISTRY,
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CCCLXXX.—*Molecular Structure in Solution. Part III. The Electrical Conductivities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid, with a Note on the Prediction of Crystal Structure.*

By Owen Rhys Howell.

The densities, viscosities, refractive indices, and surface tensions of a series of solutions containing a constant amount of cobalt chloride with increasing amounts of hydrochloric acid, and the same properties of an exactly similar series of solutions of hydrochloric acid alone have already been determined (this vol., pp. 158, 2039). The differences in the values of each of these properties for corresponding members of the two series throw light upon the change in the state of the cobalt atom in solution with increasing acid concentration. All the results obtained have been fully interpreted by assuming that, in accordance with the theory of the colour of the cobaltous compounds suggested by Hill and Howell (*Phil. Mag.*, 1924, **48**, 833), the cobalt atom is forced out of its association with 6 molecules of water into one with 4 atoms of chlorine.

The electrical conductivities of these solutions have now been examined, and the conclusions drawn from the results are in complete accord with those already indicated.

Experimental.

Determination of Electrical Conductivity.—The electrical conductivities were determined in the usual way by the use of a standard resistance, an alternating current from a small coil, a metre bridge, and a low-resistance telephone. A small **U**-shaped cell made of resistance glass and having a capacity of about 3 c.c. was employed. It was immersed to below the level of the solution in a thermostat at 20° ± 0·02°. With each solution at least three different known resistances were employed and the point of balance was determined at least four times for each. With each known resistance the mean point of balance was taken and the conductance of the cell calculated. In almost every instance, the values lay within 0·05% of the mean, and in no case did the difference exceed 0·1%.

The cell constant was determined with *N*-potassium chloride solution, prepared from the pure salt (Kahlbaum's), which was first recrystallised and dried. The conductivity of this solution at 20° is 0·10207 mho (Kohlrausch, Holborn, and Diesselhorst, *Wied. Ann.*, 1898, **64**, 417); the actual resistance was found to be 3028

ohms, whence the conductance was 0·0003302 mho and the cell constant 309·1.

Materials.—The solutions used for these determinations were the same as those employed for the measurement of the refractive index and surface tension (*loc. cit.*). A few new solutions were also prepared from the same stock solutions as those previously employed. The water used for preparing these solutions was twice redistilled; its conductivity was negligible compared with that of any of the solutions.

Results.

Conductivities.—The conductivities of the series of solutions of hydrochloric acid alone are given in column 3 of Table I. Previous measurements for concentrated solutions of hydrochloric acid have been made at 18° by Kohlrausch (*Pogg. Ann.*, 1876, **159**, 233) and at 25° by Masson and Green (J., 1908, **93**, 2023). Direct comparison with these is not possible because of the different temperatures employed, but the curve of the values now given lies smoothly between those of the other observers. The values of the conductivity are plotted against the normality of the acid (at 18°) in Fig. 1 (upper curve).

TABLE I.

Electrical Conductivities.

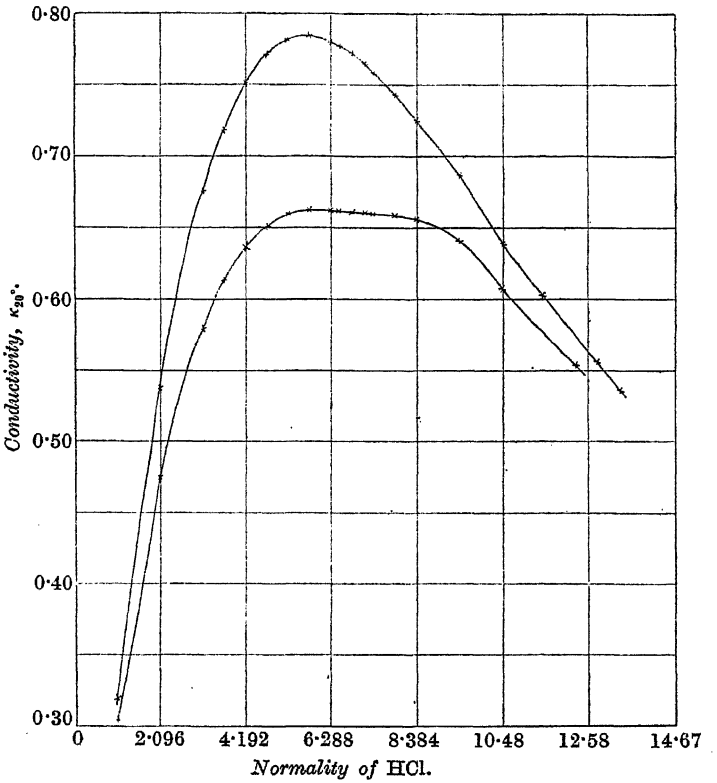
1. Normality of HCl, $N_{18°}$.	2. Conductivity of $CoCl_2$+HCl, $\kappa_{20°}$.	3. Conductivity of HCl alone, $\kappa_{20°}$.	4. Diff., 2—3.	1. Normality of HCl, $N_{18°}$.	2. Conductivity of $CoCl_2$+HCl, $\kappa_{20°}$.	3. Conductivity of HCl alone, $\kappa_{20°}$.	4. Diff., 2—3.
0	0·06358	—	+0·0636	6·812	0·6611	0·7728	−0·1117
1·048	0·3053	0·3196	−0·0143	7·126	0·6605	0·7647	−0·1042
2·096	0·4742	0·5375	−0·0633	7·336	0·6599	0·7585	−0·0986
3·144	0·5797	0·6760	−0·0963	7·860	0·6584	0·7434	−0·0850
3·668	0·6132	0·7190	−0·1058	8·384	0·6556	0·7258	−0·0702
4·192	0·6361	0·7508	−0·1147	9·432	0·6408	0·6874	−0·0466
4·716	0·6503	0·7715	−0·1212	10·48	0·6068	0·6389	−0·0321
5·240	0·6599	0·7823	−0·1224	11·48	—	0·6021	—
5·764	0·6624	0·7854	−0·1230	12·26	0·5530	0·5749	−0·0219
6·288	0·6624	0·7799	−0·1175	12·83	—	0·5564	—
6·498	0·6618	0·7771	−0·1153	13·38	—	0·5357	—

The results obtained with the series of solutions of cobalt chloride and hydrochloric acid are given in column 2 of Table I, and plotted against the normality of the acid in Fig. 1 (lower curve). The two curves are very different in form: that for the acid only rises to a sharp maximum, whereas that for the solutions containing cobalt is greatly flattened at its maximum.

The differences in conductivity between corresponding solutions in the two series are given in col. 4 of Table I and are plotted against

the normality of the acid in Fig. 2. It is seen that the conductivity-differences curve is almost the exact complement of the viscosity-differences curve, which is also reproduced for comparison; the minimum of the one occurs at the same concentration of acid as the maximum of the other. There is one point of difference, *viz.*, that whereas the viscosity-differences curve first falls slightly

FIG. 1.



Upper curve: Solutions of hydrochloric acid only.
Lower curve: Solutions of hydrochloric acid + cobalt chloride.

before rising to its maximum, the conductivity-differences curve falls continuously to its minimum. The same reasoning which accounted for the form of the first (this vol., p. 168) also explains that of the second, including this respect in which they differ.

The effect of increasing the concentration of acid is to throw more and more of the cobalt out of its association with 6 molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, into one with 4 atoms of chlorine, $CoCl_4^{\prime\prime}$. When this transition is complete, continued increase in the con-

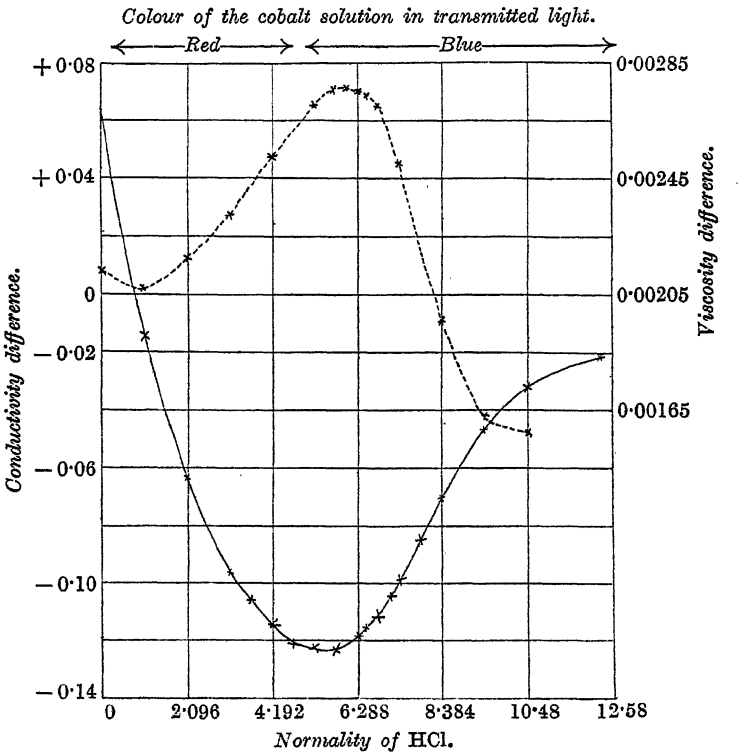
centration of acid would be without further effect, and the difference in physical properties between the solutions containing cobalt and the corresponding solutions of acid alone should become and remain constant. It is seen that the conductivity-differences curve, like the viscosity-differences curve, flattens out at the highest concentrations of acid to become parallel to the axis of concentration, indicating that this transition is practically complete. Moreover, both curves exhibit this characteristic at approximately the same concentration of acid.

It is seen that the conductivity differences at the end of the series (blue solutions) are smaller than those at the beginning (red solutions). The curve does not, however, fall evenly from the initial to the final value, but exhibits a very deep minimum, just as the viscosity-differences curve similarly shows a well-defined maximum. Since the red and the blue ions, $Co(H_2O)_6^{\cdot\cdot}$ and $CoCl_4''$, are oppositely charged, there will undoubtedly be combination between them where they are present together in solution; they will not remain wholly as free ions. The combination of these ions will result in further dissociation of the compounds from which they are derived, thus liberating chlorine ions and hydrogen ions respectively. These, however, will not remain free, the ionisation being depressed by the hydrochloric acid already present in high concentration, so that the conductivity of the solution will diminish. The greater the combination, the less will be the conductivity of the solution; therefore, as transformation of the red $Co(H_2O)_6^{\cdot\cdot}$ into the blue $CoCl_4''$ proceeds, the conductivity-differences curve falls sharply. The combination will evidently be greatest when these two oppositely charged ions are present in equal amounts, so that the conductivity differences should decrease up to this point. Thereafter, continued transformation of the $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions will result in an increasing surplus of free $CoCl_4''$ and the conductivity differences should increase again up to a constant value. This is seen to be so and it is therefore suggested that the minimum of the conductivity-differences curve occurs when half the cobalt is present as $Co(H_2O)_6^{\cdot\cdot}$ and half as $CoCl_4''$.

The viscosity-differences curve exhibits an initial decrease before rising to its maximum, whereas the conductivity-differences curve falls sharply to its minimum. When discussing the viscosity-differences curve (*loc. cit.*), it was pointed out that the first effect of the addition of hydrochloric acid is to depress the ionisation of the cobalt chloride because of the addition of a common ion. There is thus at first a decrease in the number of the viscous $Co(H_2O)_6^{\cdot\cdot}$ ions, resulting in a decrease of viscosity. This effect is soon overwhelmed by the conversion of $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions,

so that the curve exhibits only a small dip and then rises rapidly. The two effects are thus opposed when the viscosity of the solutions is concerned; but they operate together when the conductivity is considered. Both the initial depression of ionisation and (as discussed above) the conversion of $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions result in a decrease of conductivity, so that the conductivity-differences curve falls continuously to its minimum.

FIG. 2.



Full curve: Conductivity differences.
Broken curve: Viscosity differences.

It may readily be shown that the curve of the differences of specific resistance is quite different in form from that of the differences of specific conductance. It is very similar to the density-differences and refractive-index-differences curves found previously (*loc. cit.*), in that it exhibits a point of inflexion at the same concentration of acid and then falls, eventually becoming parallel to the axis of concentration, just as these do, and at about the same concentration of acid. It differs from them in first rising to a

maximum, whereas they fall continuously from the beginning; and this difference is explained in exactly the same way as that between the conductivity-differences and viscosity-differences curves.

Note on the Prediction of Crystal Structure.

When the metallic atom of a colourless insoluble compound is replaced, wholly or partly, by cobalt, a pigment is obtained which may be either blue or red, and it has been shown (Hill and Howell, *loc. cit.*), by carrying out this replacement in compounds of known crystal structure, that when the metallic atom is surrounded by *four* other atoms or groups, the resulting pigment is *blue*, and when surrounded by *six*, the pigment obtained is *red*. Thus, when the magnesium atom in spinelle (magnesium aluminate, where it is surrounded by four oxygen atoms) is replaced by cobalt, a blue pigment (cobalt blue) is obtained, but when the magnesium atom in magnesium oxide (where it is surrounded by six oxygen atoms) is similarly replaced, a red pigment (cobalt pink) is produced.

For comparison of their absorption spectra, pigments were prepared, not only from compounds of known crystal structure, but also from a number the structure of which was at that time unknown. From the colour of the pigment obtained, it was possible to predict the structure of the compound from which it was derived. Since that work was published, two of the compounds have been submitted to *X*-ray analysis by different observers, and the structure is in both instances in accord with that predicted from the colour of the corresponding cobalt pigment. The structures of cobalt oxide and cobalt fluoride have also been subsequently determined and are in agreement with the predictions from the theory.

Zinc orthosilicate. If the zinc atom in zinc orthosilicate is replaced by cobalt, a *blue* pigment is obtained. It follows from the theory that in the pigment the cobalt atom is surrounded by *four* other atoms or groups, and therefore that the zinc atom in the original compound is similarly situated. The crystal structure of willemite (zinc orthosilicate) has recently been determined by Zachariasen (*Norsk. Geol. Tidsskr.*, 1926, **9**, 65), who showed it to be isomorphous with phenacite (beryllium orthosilicate), the crystal structure of which was elucidated by W. L. Bragg (*Proc. Roy. Soc.*, 1927, *A*, **113**, 642), who established that the beryllium atom is between four oxygen atoms. It follows that in zinc orthosilicate the zinc atom is similarly placed, as predicted from the theory.

Magnesium orthosilicate. If the magnesium atom in magnesium orthosilicate is replaced by cobalt, a *red* pigment is produced, so that, according to the theory, the magnesium atom in this compound is surrounded by *six* other atoms. This prediction has been verified

by the work of W. L. Bragg and Brown (*Z. Krist.*, 1926, **63**, 538) on olivine (magnesium orthosilicate).

Cobalt oxide. It is well known that when cobalt oxide is melted in the electric furnace, it crystallises in rose-coloured needles (Moissan, *Compt. rend.*, 1892, **115**, 1034; *Bull. Soc. chim.*, 1893, **9**, 955; *Ann. Chim. Phys.*, 1895, **4**, 136). Although the crystal structure of the compound was unknown, the theory enabled us to predict that, since the compound was of the *red* form, the cobalt atom should be surrounded by *six* oxygen atoms, and verification was forthcoming in the work of Goldschmidt, Barth, and Lunde (*Skrifter Norske Videnskaps Akad.*, No. 7, 1925), of Natta and Reina (*Atti R. Accad. Lincei*, 1926, **4**, 48), and of Bravo (*Anal. Fís. Quím.*, 1926, **24**, 611), who found that the compound possesses the rock-salt structure, *i.e.*, the cobalt atom is between six oxygen atoms.

Cobalt fluoride. Since anhydrous cobaltous fluoride is *red* (Poulenc, *Compt. rend.*, 1892, **114**, 1426), it could be predicted that the cobalt atom should lie between *six* fluorine atoms. Actually, it has been found (Ferrari, *Atti R. Accad. Lincei*, 1926, **3**, 324) to have the same crystal structure as rutile, in which the titanium atom is surrounded by six oxygen atoms (Vegard, *Phil. Mag.*, 1916, **32**, 65, 505; 1917, **33**, 395; 1926, **1**, 1151; Williams, *Proc. Roy. Soc.*, 1917, **93**, 418; Greenwood, *Phil. Mag.*, 1924, **48**, 654).

Summary.

1. The electrical conductivities of a series of solutions containing a constant amount of cobalt chloride and increasing amounts of hydrochloric acid have been determined.

2. The same properties of an exactly similar series containing hydrochloric acid only have also been determined.

3. The curve of the differences of conductivity of corresponding solutions plotted against the concentration of acid is almost the exact complement of the viscosity-differences curve found in a previous investigation. It exhibits a minimum at the same concentration of acid where the other curve exhibits a maximum. It differs in falling constantly to the minimum, whereas the viscosity-differences curve first falls slightly before rising to its maximum. Both its resemblance to and difference from the viscosity-differences curve are fully explained on the same reasoning as that employed in previous investigations.

4. It is noted that the crystal structure of compounds which yield pigments when the metallic atom is replaced by cobalt can be predicted from the colour of the pigment so obtained. The structures of two compounds (zinc and magnesium orthosilicates) have been determined since the theory of the colour of the cobaltous

compounds was suggested, and they verify the predictions made from the theory. The structures of cobalt oxide and cobalt fluoride are similarly in accordance with prediction from the theory.

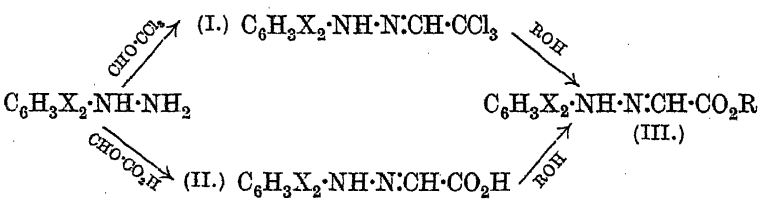
The author would again express his thanks to Prof. F. L. Pyman, F.R.S., for giving him every facility for doing this work.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, September 1st*, 1927.]

CCCLXXXI.—*The Interaction of Chloral and Arylhydrazines.*

By FREDERICK DANIEL CHATTAWAY and RANDLE BENNETT.

OWING to the violence with which the hydrazone initially formed decomposes, the behaviour of chloral with phenylhydrazine has been little studied. When, however, a 2 : 4-dihalogen-substituted phenylhydrazine is used, the decomposition occurs more quietly and the final products can be isolated. These differ according to the nature of the solvent in which interaction occurs. When any alcohol is used as the solvent, the 2 : 4-dihalogen-substituted phenylhydrazone of the corresponding alkyl glyoxylate (III) is produced identical with the ester yielded by the corresponding dihalogen-substituted phenylhydrazone of glyoxylic acid :



Bromal behaves in an exactly similar manner, although the reaction is not so vigorous as when chloral is used.

When, on the other hand, interaction takes place in water or acetic acid, one molecule of water and one molecule of hydrogen chloride are eliminated and beautifully crystalline, brilliant red compounds formed. When strongly reduced, these yield 2 : 4-dihalogen-substituted aniline; the chlorine atom lost in the decomposition must therefore be one of those contained in the chloral. They are unaffected by heating with acetic anhydride, whilst their intense red colour recalls that of compounds containing an azo-group. Bromine replaces one hydrogen atom not in the nucleus, the substitution product still retaining its red colour.

These red compounds therefore appear to be αα-dichloro-β-2 : 4-dihalogenobenzeneazoethylenes (IV), and the bromine substitution products αα-dichloro-β-bromo-β-2 : 4-dihalogenobenzeneazoethylenes (V), formed thus :

(I.) ⟶ (IV.) $C_6H_3X_2{\cdot}N{:}N{\cdot}CH{:}CCl_2$ ⟶ (V.) $C_6H_3X_2{\cdot}N{:}N{\cdot}CBr{:}CCl_2$.

When the azoethylenes are heated with alcohols they are converted into the corresponding alkyl glyoxylate arylhydrazones (III), but the reaction is not so rapid as that by which the latter compounds are formed from the chloral hydrazones.

EXPERIMENTAL.

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Ethyl Alcohol.*—When 21·5 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) and 16·5 g. of chloral hydrate (1 mol.) were added to 100 c.c. of ethyl alcohol, the liquid became yellow, but little action appeared to take place at the ordinary temperature. On heating, the colour deepened to dark orange and at about 60° hydrogen chloride was evolved, much heat liberated, and the liquid boiled spontaneously for several minutes. The bulk of the alcohol was then slowly distilled off; the residual clear deep yellow liquid, on cooling, deposited bright yellow crystals of *ethyl glyoxylate* 2 : 4-*dichlorophenylhydrazone*, the yield being practically theoretical. This substance is easily soluble in warm alcohol and separates in pale yellow, very slender prisms, m. p. 121·5° (Found : C, 45·8; H, 3·8; N, 11·1; Cl, 27·2. $C_{10}H_{10}O_2N_2Cl_2$ requires C, 46·0; H, 3·8; N, 10·8; Cl, 27·2%). It yielded ethyl alcohol and glyoxylic acid 2 : 4-dichlorophenylhydrazone on hydrolysis, and 2 : 4-dichloroaniline on reduction.

Methyl glyoxylate 2 : 4-*dichlorophenylhydrazone* crystallises in pale yellow, slender prisms, m. p. 136·5° (Found : C, 43·9; H, 3·4; Cl, 28·8. $C_9H_8O_2N_2Cl_2$ requires C, 43·7; H, 3·2; Cl, 29·0%), n-*propyl glyoxylate* 2 : 4-*dichlorophenylhydrazone* in short, pale yellow, flattened prisms, m. p. 65° (Found : Cl, 25·6. $C_{11}H_{12}O_2N_2Cl_2$ requires Cl, 25·8%), and n-*butyl glyoxylate* 2 : 4-*dichlorophenylhydrazone* in slender, yellow, flattened prisms, m. p. 59° (Found : Cl, 24·3. $C_{12}H_{14}O_2N_2Cl_2$ requires Cl, 24·5%).

Action of 2 : 4-*Dibromophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Methyl Alcohol.*—2 : 4-Dibromophenylhydrazine hydrochloride (15 g.; 1 mol.), chloral hydrate (8 g.; 1 mol.), and methyl alcohol (60 c.c.), when heated together under reflux on a water-bath for an hour, reacted vigorously with liberation of hydrogen chloride. A deep yellow liquid was obtained, from which *methyl glyoxylate* 2 : 4-*dibromophenylhydrazone* separated on cooling.

It crystallises from boiling methyl alcohol, in which it is moderately easily soluble, in slender, pale yellow, flattened prisms, m. p. 136° (Found: C, 32·2; H, 2·5; Br, 47·6. $C_9H_8O_2N_2Br_2$ requires C, 32·1; H, 2·4; Br, 47·6%).

Similar esters were obtained when chloral was allowed to interact with 2 : 4-dibromophenylhydrazine, 2-chloro-4-bromophenylhydrazine, and 4-chloro-2-bromophenylhydrazine in presence of alcohols and were all found to be identical with the corresponding esters prepared from glyoxylic acid.

Ethyl glyoxylate 2 : 4-*dibromophenylhydrazone* crystallises in slender, pale yellow, flattened prisms, m. p. 119° (Found: Br, 45·6. $C_{10}H_{10}O_2N_2Br_2$ requires Br, 45·7%), n-*propyl glyoxylate* 2 : 4-*dibromophenylhydrazone* in short, pale yellow, flattened prisms, m. p. 75° (Found: Br, 44·0. $C_{11}H_{12}O_2N_2Br_2$ requires Br, 43·9%), and *ethyl glyoxylate* 2-*chloro*-4-*bromophenylhydrazone* (Found: Cl, 11·6; Br, 26·3. $C_{10}H_{10}O_2N_2ClBr$ requires Cl, 11·6; Br, 26·2%) and *ethyl glyoxylate* 4-*chloro*-2-*bromophenylhydrazone* in slender, pale yellow prisms, m. p. 120° and 115°, respectively.

Glyoxylic Acid 2 : 4-*Dichlorophenylhydrazone*.—Glyoxylic acid (made by the electrolytic reduction of oxalic acid) and 2 : 4-dichlorophenylhydrazine hydrochloride reacted at once in aqueous solution at 60° and the *hydrazone* separated as a yellow solid. It is sparingly soluble in water, very easily soluble in alcohol, and crystallises from hot aqueous alcohol in pale yellow needles, decomp. about 150° (Found: Cl, 30·3. $C_8H_6O_2N_2Cl_2$ requires Cl, 30·4%).

The 2 : 4-*dibromophenylhydrazone* of glyoxylic acid resembles the dichloro-hydrazone very closely. It crystallises in pale yellow needles, decomp. about 150° (Found: Br, 49·5. $C_8H_6O_2N_2Br_2$ requires Br, 49·7%).

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Bromal dissolved in Ethyl Alcohol*.—A mixture of 11 g. of 2 : 4-dichlorophenylhydrazine hydrochloride, 14 g. of bromal, and 100 c.c. of ethyl alcohol was boiled under reflux for an hour, hydrogen bromide being liberated in quantity and ethyl bromide (recognisable by its odour) formed. The bright yellow liquid obtained, on cooling, deposited ethyl glyoxylate 2 : 4-dichlorophenylhydrazone, m. p. 121·5°, identical in every respect with that prepared both from chloral and from glyoxylic acid.

Methyl glyoxylate 2 : 4-dibromophenylhydrazone, m. p. 136°, was similarly obtained when 2 : 4-dibromophenylhydrazine hydrochloride was heated with bromal dissolved in methyl alcohol.

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Acetic Acid or Water*.—To a solution of 16·5 g. (1 mol.) of chloral hydrate in 100 c.c. of acetic acid, 21·5 g. (1 mol.)

of 2 : 4-dichlorophenylhydrazine hydrochloride and 33 g. of anhydrous sodium acetate (4 mols.) were added. The liquid became pale yellow, but little apparent change occurred until the temperature was raised to about 60°; obvious action then took place and the liquid became bright red. It was heated on a water-bath for ½ hour to complete the reaction and poured into water; *αα-dichloro-β-2 : 4-dichlorobenzeneazoethylene* (IV) then separated as a scarlet-red solid.

If aqueous solutions of equivalent quantities of chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride are mixed and slowly heated, the same compound separates at about 80° as a crimson, viscid liquid which solidifies on cooling and from which the supernatant liquid, now strongly acid from the hydrogen chloride set free in the reaction, can be decanted.

The red solid is readily soluble in boiling chloroform, acetic acid, and alcohol, and separates from warm alcohol in slender, flattened, golden-red prisms, m. p. 84·5° (Found : C, 35·6; H, 1·6; N, 10·2; Cl, 52·5; *M*, cryoscopic in benzene, 262. $C_8H_4N_2Cl_4$ requires C, 35·6; H, 1·5; N, 10·4; Cl, 52·6%; *M*, 270). It does not react with acetic anhydride. When it was boiled with ethyl alcohol for 8 hours, a deep orange-coloured liquid was obtained from which, on cooling, ethyl glyoxylate 2 : 4-dichlorophenylhydrazone separated.

Action of Bromine upon αα-Dichloro-β-2 : 4-dichlorobenzeneazoethylene.—To a solution of 5 g. (1 mol.) of αα-dichloro-β-2 : 4-dichlorobenzeneazoethylene in 20 c.c. of warm acetic acid, 3·5 g. (1 mol.) of bromine in 5 c.c. of acetic acid were added. The bromine slowly disappeared and the solution became paler in colour. The solution was then poured into water; *αα-dichloro-β-bromo-β-2 : 4-dichlorobenzeneazoethylene* (V) separated as a brownish-red solid. It is easily soluble in warm acetic acid or alcohol and separates in small, red needles, m. p. 90° (Found : Cl, 40·5; Br, 22·7. $C_8H_3N_2Cl_4Br$ requires Cl, 40·7; Br, 22·9%).

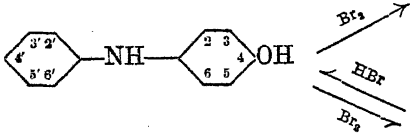
αα-Dichloro-β-2 : 4-dibromobenzeneazoethylene crystallises in slender, orange-red, flattened prisms, m. p. 96·5° (Found : Cl, 19·9; Br, 44·9. $C_8H_4N_2Cl_2Br_2$ requires Cl, 19·8; Br, 44·6%), *αα-dichloro-β-2-chloro-4-bromobenzeneazoethylene* in small, slender, orange-red prisms, m. p. 84° (Found : Cl, 33·6; Br, 25·3. $C_8H_4N_2Cl_3Br$ requires Cl, 33·8; Br, 25·4%), and *αα-dichloro-β-4-chloro-2-bromobenzeneazoethylene* in slender, orange-red prisms, m. p. 81°.

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CCCLXXXII.—*The Halogenation of* p-*Hydroxydiphenylamine. Part II.*

By Alan Edwin Bradfield, Leslie Hugh Norman Cooper, and Kennedy Joseph Previté Orton.

The main reaction between bromine or chlorine and *p*-hydroxydiphenylamine and its derivatives (Smith and Orton, J., 1908, **93**, 314) may follow one of two paths, leading either to a halogen-substituted *p*-hydroxydiphenylamine (A) or to a quinoneanil (benzoquinonephenylimine) (B). More drastic treatment leads to a disruption of the molecule.



$$C_{12}H_{10}NOBr + HBr \quad (A)$$

$$C_6H_5{\cdot}N{:}C_6H_4{:}O + 2HBr \quad (B)$$

The bromination of *p*-hydroxydiphenylamine, which is very rapid (*loc. cit.*), indicates that the imino-group is much more powerful as a directing group than the hydroxyl, the 2 : 2′ : 4′-trisubstituted compound being the first isolable product. The influence of the imino-group is then diminished and bromine enters successively into positions 5 and 3, and, finally, positions 6 and 6′ simultaneously. It is now found that, when the hydroxyl group is previously esterified by means of benzoyl chloride or *p*-toluenesulphonyl chloride, the 4′-bromo-, 2 : 2′ : 4′-tribromo-, and, finally, 2 : 6 : 2′ : 4′ : 6′-pentabromo-compounds are successively obtained.

In acetic acid, the first main action of bromine on 2 : 6 : 2′ : 4′ : 6′-pentabromohydroxydiphenylamine is oxidation to the quinoneanil. The reaction is reversible and, provided the hydrogen bromide formed is not removed, an equilibrium is reached. The small amount of the hydroxy-compound present undergoes slow nuclear substitution (irreversible), displacing the equilibrium, and in time the whole is converted into the 2 : 3 : 5 : 6 : 2′ : 4′ : 6′-heptabromohydroxy-derivative, the original violet colour of the solution fading as the quinoneanil is reduced by the hydrogen bromide and brominated. If the hydrogen bromide be removed by the addition of sodium acetate, reduction and bromination are prevented.

Chlorine has a disruptive action on *p*-hydroxydiphenylamine; the benzoate or *p*-toluenesulphonate, however, may be chlorinated by the chloroamine method (Orton and King, J., 1911, **99**, 1185; Orton and Bradfield, this vol., p. 986), the reaction following a similar

course to that of bromination of the esters, yielding finally the 2 : 6 : 2′ : 4′ : 6′-pentachloro-compound. The rate of further substitution in 2 : 6 : 2′ : 4′ : 6′-pentachloro-*p*-hydroxydiphenylamine, obtained from the ester, has now become so diminished that when it is treated with chlorine, oxidation to the quinoneanil initially predominates. This is succeeded, however, by reduction and substitution as in the further bromination of pentabromohydroxydiphenylamine, yielding the 2 : 3 : 6 : 2′ : 4′ : 6′-hexachloro- and 2 : 3 : 5 : 6 : 2′ : 4′ : 6′-heptachloro-derivatives.

The action of hydrochloric acid on an acetic acid solution of the pentachloroquinoneanil obtained by oxidation of pentachlorohydroxydiphenylamine with chromic anhydride or mercuric oxide yields the same hexa- and hepta-chloro-compounds. This fact is entirely in harmony with the view of the course of the reaction of *p*-hydroxydiphenylamine derivatives with halogens which has been put forward above; in so far as it relates to the production of halogenated derivatives from the quinoneanil, it closely resembles the scheme first advanced by Wichelhaus (*Ber.*, 1879, **12**, 1500) to explain the action of hydrochloric acid on quinone.

Several mixed chlorobromo-*p*-hydroxydiphenylamine derivatives have been prepared.

Amongst the properties of the halogen derivatives of *p*-hydroxydiphenylamine, certain anomalies appear for which at present no explanation can be offered. These are:

(1) The majority of the compounds are, as would be expected, soluble in aqueous alkali; but the following are not, although they are soluble in alcoholic potash: 2 : 2′ : 4′-trichloro-5 : 6′-dibromo-, 2 : 5 : 2′ : 4′-tetrabromo-, 2 : 2′ : 4′-trichloro-3 : 5 : 6 : 6′-tetrabromo-, 2 : 3 : 5 : 2′ : 4′-pentabromo-, 2 : 3 : 5 : 2′ : 4′ : 6′-hexabromo-, 2 : 3 : 5 : 2′ : 4′ : 6′-hexachloro- and heptabromo-*p*-hydroxydiphenylamine.

Further, these same compounds have resisted all attempts at sulphonylation with *p*-toluenesulphonyl chloride, not only by the Schotten–Baumann procedure, but in pyridine or quinoline, in which they are soluble, indicating that the phenomenon, although concomitant, is not attributable simply to insolubility.

(2) Although 2 : 5 : 2′ : 4′-tetrabromo- and 2 : 3 : 5 : 2′ : 4′-pentabromo-*p*-hydroxydiphenylamine react with bromine, the benzoyloxy-derivatives prepared from them react very slowly or not at all under the conditions usually successful, in spite of the fact that positions ortho to the imino-group remain vacant, *i.e.*, esterification not only retards substitution in the ortho-position to the hydroxyl group, but greatly diminishes the reactivity of the molecule as a whole, even transmitting the effect through nitrogen to an attached

benzene ring. It is hoped to study this observation, which appears to be unique, in greater detail.

EXPERIMENTAL.

In the preparation of *p*-hydroxydiphenylamine by Calm's method (*Ber.*, 1883, **16**, 2786; 1884, **17**, 2431) the yield is much improved by the employment of crude aniline, and both yield and purity are enhanced if pure aniline to which a drop of sulphuric acid has been added is used. The product, after distillation in superheated steam and then under 12 mm. pressure, melts at 73°.

The p-*toluenesulphonyl* derivative, prepared from *p*-toluenesulphonyl chloride (210 g.), *p*-hydroxydiphenylamine (185 g.), benzene (900 c.c.), and aqueous sodium hydroxide, crystallises from alcohol in thin plates, m. p. 126·5°, soluble in benzene and chloroform, less soluble in alcohol, petroleum, and acetic acid (Found: S, 9·5. $C_{19}H_{17}O_3NS$ requires S, 9·5%).

The acetic acid used as a medium for halogenation was purified by Orton and Bradfield's method (this vol., p. 983).

Chloro-compounds.

The following chloro-4-acyloxydiphenylamines were prepared by chlorination by the chloroamine (*N* : 2 : 4-trichloroacetanilide or dichloramine T) method and were usually precipitated on addition of water. They were hydrolysed by boiling alcoholic potassium hydroxide, and the hydroxy-compounds precipitated by addition of water to the acidified solutions. The anils were prepared by oxidising the corresponding chlorohydroxydiphenylamines in boiling benzene with yellow mercuric oxide or in boiling acetic acid with chromic acid; they were usually isolated by evaporation of the solvent and addition of petroleum in the former method and by addition of water in the latter. Fission of the anils was effected in acetic acid by addition of sulphuric acid; on dilution with water and basification, the expected chloroaniline was obtained in every case.

4′-*Chloro*-4-*benzoyloxydiphenylamine* is prepared from *p*-benzoyloxydiphenylamine; the reaction, initiated by the addition of one drop of hydrochloric acid, is completed in 15 minutes. The product (yield, 30%) crystallises from petroleum or 98% acetic acid in silvery plates, m. p. 148·5°. The presence of isomerides is indicated (Found: Cl, 10·6. $C_{19}H_{14}O_2NCl$ requires Cl, 11·0%).

4′-*Chloro*-4-*hydroxydiphenylamine* forms pale green leaflets (yield, 72%), m. p. 91° (Found: Cl, 15·9. $C_{12}H_{10}ONCl$ requires Cl, 16·2%). The p-*toluenesulphonate* has m. p. 93—94° (Found: Cl, 9·3. $C_{19}H_{16}O_3NClS$ requires Cl, 9·5%).

4′-*Chlorobenzoquinoneanil* crystallises in dark red, massive prisms,

m. p. 83·5°, insoluble in water, sparingly soluble in alcohol, hot or cold, and in cold petroleum and acetic acid, readily soluble in chloroform and benzene (Found: Cl, 16·0. $C_{12}H_8ONCl$ requires Cl, 16·3%).

2 : 2′ : 4′-*Trichloro*-4-*benzoyloxy*- and -4-p-*toluenesulphonyloxy*-*diphenylamines* are prepared at 50—55° from the 4-acyloxy-compounds or their monochloro-derivatives and separate on cooling. The *benzoyloxy*-compound has m. p. 114° (Found: Cl, 27·3. $C_{19}H_{12}O_2NCl_3$ requires Cl, 27·1%); the *toluenesulphonyloxy*-compound crystallises from hot benzene–petroleum or from acetic acid in prisms, m. p. 130·5° (Found: Cl, 24·3. $C_{19}H_{14}O_3NCl_3S$ requires Cl, 24·1%).

2 : 2′ : 4′-*Trichloro*-4-*hydroxydiphenylamine*, crystallised from glacial acetic acid and then from petroleum, forms prisms, never quite colourless, m. p. 128° (Found: Cl, 36·7. $C_{12}H_8ONCl_3$ requires Cl, 36·9%).

2 : 2′ : 4′-*Trichlorobenzoquinoneanil* separates from petroleum (b. p. 40—60°), containing a very little benzene, in long, bronzy needles, m. p. 72·5°. It is readily soluble in all organic solvents except light petroleum (Found: Cl, 37·1. $C_{12}H_6ONCl_3$ requires Cl, 37·2%).

2 : 6 : 2′ : 4′-*Tetrachloro*-4-p-*toluenesulphonyloxydiphenylamine* is obtained from the trichlorotoluenesulphonyloxydiphenylamine at 45—50°, and is separated from the other isomerides produced only by a tedious series of fractional precipitations from chloroform and light petroleum. It is much more soluble in common solvents than the tri- and penta-chloro-derivatives, and crystallises from acetic acid, chloroform, and petroleum (b. p. 110°) in prisms, m. p. 126° (Found: Cl, 30·1. $C_{19}H_{13}O_3NCl_4S$ requires Cl, 29·8%).

The *tetrachlorohydroxy*-compound solidifies with difficulty, but after being thoroughly washed and dried it may be obtained crystalline by the addition of petroleum, b. p. 40—60°, to a solution in petroleum, b. p. 110°; it then melts at 113° (Found: Cl, 44·3. $C_{12}H_7ONCl_4$ requires Cl, 44·0%). The *tetrachlorobenzoyloxy*-compound is obtained by benzoylating the tetrachlorohydroxy-compound in pyridine; after crystallisation from petroleum (b. p. 60—85°) it melts at 114·5° (Found: Cl, 33·1. $C_{19}H_{11}O_2NCl_4$ requires Cl, 33·3%).

2 : 6 : 2′ : 4′-*Tetrachlorobenzoquinoneanil* separates from ethyl acetate in violet crystals, m. p. 143° (Found: Cl, 44·5. $C_{12}H_5ONCl_4$ requires Cl, 44·2%).

2 : 6 : 2′ : 4′ : 6′-*Pentachloro*-4-*benzoyloxydiphenylamine* is prepared from the mono- or trichloro-derivative; after crystallisation from alcohol (yield, 62%) it melts at 133—134° (Found: Cl, 38·0. $C_{19}H_{10}O_2NCl_5$ requires Cl, 38·4%). The *toluenesulphonyloxy*-compound is prepared from the trichlorosulphonyloxy-compound

at 55°; on cooling, it separates in quantitative yield, in prisms, m. p. 156·5°, unaltered by crystallisation from acetic acid. It is also obtained by passing chlorine into a hot acetic acid solution of 4-*p*-toluenesulphonyloxydiphenylamine in presence of anhydrous sodium acetate. It is soluble in chloroform, but sparingly soluble in other solvents (Found: Cl, 34·7. $C_{19}H_{12}O_3NCl_5S$ requires Cl, 34·7%). The *pentachlorohydroxy*-compound crystallises from petroleum in clear brown prisms, m. p. 156° (Found: Cl, 49·2. $C_{12}H_6ONCl_5$ requires Cl, 49·6%). The *monoacetyl* derivative, obtained by treating the hydroxy-compound in acetic acid with acetic anhydride in the presence of sodium acetate, has m. p. 126°. It is insoluble in alkali, very soluble in benzene, petroleum, and chloroform, and sparingly soluble in acetic acid (Found: Cl, 44·0. $C_{14}H_8O_2NCl_5$ requires Cl, 44·4%).

2 : 6 : 2′ : 4′ : 6′-*Pentachlorobenzoquinoneanil* (prepared by the chromic acid method) forms fine, bronzy-red needles with a metallic lustre, m. p. 163° (Found: Cl, 49·5. $C_{12}H_4ONCl_5$ requires Cl, 49·9%).

All attempts to chlorinate further *p*-benzoyloxy- and 4-*p*-toluenesulphonyloxy-diphenylamine have been unsuccessful, as is to be expected.

2 : 3 : 6 : 2′ : 4′ : 6′-*Hexachloro*-4-*hydroxydiphenylamine* is prepared from pentachlorohydroxydiphenylamine and forms hemispherical nodules, m. p. 114° (Found: Cl, 53·6. $C_{12}H_5ONCl_6$ requires Cl, 54·3%). Benzoylation in pyridine gives the *benzoyloxy*-derivative, which, crystallised from alcohol and then from petroleum, forms small clusters of hard, glistening, brown prisms, m. p. 125° (Found: Cl, 42·5. $C_{19}H_9O_2NCl_6$ requires Cl, 42·9%). The *toluenesulphonyloxy*-derivative crystallises from glacial acetic acid in white prisms, m. p. 141° (Found: Cl, 39·0. $C_{19}H_{11}O_3NCl_6S$ requires Cl, 39·0%).

2 : 3 : 6 : 2′ : 4′ : 6′-*Hexachlorobenzoquinoneanil** is obtained by the

* The synthesis of this compound establishes the hitherto uncertain constitution of the isomeride yielding the same fission products which was obtained by Orton and Smith (J., 1905, **87**, 389) as a product of the transformation of *s*-trichlorophenylnitroamine, as the 2 : 3 : 5 : 2′ : 4′ : 6′-compound. Similarly, the preparation of 2 : 6 : 2′ : 4′ : 6′-pentabromobenzoquinoneanil (p. 2861) establishes the constitution of the isomeride produced by transformation of *s*-tribromophenylnitroamine (Orton and Smith, J., 1907, **91**, 146) as the 3 : 5 : 2′ : 4′ : 6′-pentabromo-compound. It is regretted that, owing to a clerical error, the melting points of the penta- and hexa-bromobenzoquinoneanils given in that paper have become interchanged. Further examination has shown that the hexabromoquinoneanil then obtained was not completely pure. The following corrected melting points are given to avoid ambiguity:

3 : 5 : 2′ : 4′ : 6′-Pentabromo-4-hydroxydiphenylamine, m. p. 157°.
3 : 5 : 2′ : 4′ : 6′-Pentabromobenzoquinoneanil, m. p. 150·5°.
2 : 3 : 5 : 2′ : 4′ : 6′-Hexabromo-4-hydroxydiphenylamine, m. p. 216°.
2 : 3 : 5 : 2′ : 4′ : 6′-Hexabromobenzoquinoneanil, m. p. 171°.

chromic acid method as a black, crystalline solid, m. p. 114° after recrystallisation from alcohol. It dissolves in ordinary solvents, except alcohol, to give violet solutions (Found: Cl, 54·2. $C_{12}H_3ONCl_6$ requires Cl, 54·65%). On treatment of the red-brown solution in sulphuric acid (1 in 100) with water, the colour changes to light yellow and a mixture of yellow plates and red needles separates. The mixture is collected and digested with a little cold alcohol; the yellow trichlorobenzoquinone remaining undissolved melts, after crystallisation from hot alcohol, at 162—163°. Careful dilution of the alcoholic extract gave *s*-trichloroaniline, m. p. 77·5° (acetyl derivative, m. p. 204°).

Heptachloro-4-hydroxydiphenylamine.—The pentachlorohydroxydiphenylamine (5 g.; 1 mol.) in 15 c.c. of acetic acid is treated with a solution of *N*-chloroacetamide (1·35 g.; 1 mol.) in 5 c.c. of the same solvent, together with two drops of 20% hydrochloric acid, the mixture becoming at once deep violet. After 1 hour, a like amount of chloroamine is added. No chlorine remains after 18 hours. The solution is decolorised by heating with zinc dust and the boiling suspension is filtered at once. White needles (55%) separate on cooling, m. p. 158—159°, unchanged on recrystallisation from petroleum or slightly diluted acetic acid (Found: Cl, 58·05. $C_{12}H_4ONCl_7$ requires Cl, 58·3%).

The *benzoyloxy*-derivative crystallises from glacial acetic acid in massive, white plates, m. p. 164° (Found: Cl, 46·5. $C_{19}H_8O_2NCl_7$ requires Cl, 46·8%). The sulphonylation of the heptachlorohydroxy-derivative is characterised by its slowness, due no doubt to the presence of two ortho-substituents. After 45 minutes' shaking, a violet solid has separated; after being washed with water and with benzene, it crystallises from glacial acetic acid in white needles, m. p. 141·5° (Found: Cl, 42·4. $C_{19}H_{10}O_3NCl_7S$ requires Cl, 42·8%).

Heptachlorobenzoquinoneanil separates from alcohol in small, black crystals, m. p. 114°. Its solutions are violet. Fission by dilute sulphuric acid (1 in 50) and addition of water gives successively tetrachlorobenzoquinone (which sublimes in pale yellow, iridescent plates, not molten at 260°) and *s*-trichloroaniline, m. p. 77·5°.

Action of Hydrochloric Acid on 2 : 6 : 2′ : 4′ : 6′-Pentachlorobenzoquinoneanil.—Concentrated hydrochloric acid (2 c.c.) was added to the quinoneanil (1·5 g.) in glacial acetic acid (100 c.c.). After 18 hours, the bluish-green solution was treated with zinc dust to remove the excess of hydrochloric acid, filtered, and diluted with 300—400 c.c. of water. Hexachlorohydroxydiphenylamine separated as white, crystalline crusts, m. p. 114° after recrystallisation. The action of hydrochloric acid on 2 : 3 : 6 : 2′ : 4′ : 6′-hexachlorobenzo-

quinoneanil in a similar manner yielded heptachlorohydroxydiphenylamine.

Bromo-compounds.

4′-Bromo-4-benzoyloxydiphenylamine. — *p*-Benzoyloxydiphenylamine (5 g.; 1 mol.) and anhydrous sodium acetate (2 mols.), dissolved in 250 c.c. of acetic acid, were treated with a solution of bromine (0·865 c.c.; 1 mol.) in 125 c.c. of acetic acid. After ½ hour, dilution to 75% caused slow separation of white, fibrous needles, which, after crystallisation from alcohol or benzene–ligroin, melted at 150·5°: yield, 33% (Found: Br, 21·2. $C_{19}H_{14}O_2NBr$ requires Br, 21·7%).

By hydrolysis of the above, the *hydroxy*-compound was obtained as thin laminæ, m. p. 108°, in 75% yield (Found: Br, 29·7. $C_{12}H_{10}ONBr$ requires Br, 30·3%).

4′-Bromobenzoquinoneanil was obtained by oxidation of the hydroxy-compound with excess of yellow mercuric oxide. The solution was evaporated to a small volume and the quinoneanil then separated in scarlet crystals, m. p. 100—104°. The melting point of this substance, which appears to be dimorphic, is not sharp and depends on the nature and temperature of the solvent (Found: Br, 29·8. $C_{12}H_8ONBr$ requires Br, 30·5%). Fission gave *p*-bromoaniline, but no trace of *p*-benzoquinone was found.

2 : 2′ : 4′-Tribromo-4-p-toluenesulphonyloxydiphenylamine was prepared, by the method described above, from 4-*p*-toluenesulphonyloxydiphenylamine at 50°, and crystallised from benzene–petroleum, acetone, or glacial acetic acid (Found: Br, 41·7; S, 5·6. $C_{19}H_{14}O_3NBr_3S$ requires Br, 41·7; S, 5·5%). The tribromo-4-benzoyloxy-compound obtained by Smith and Orton (*loc. cit.*) is produced in better yield by the Schotten–Baumann method or by bromination of *p*-benzoyloxydiphenylamine. Both esters are sparingly soluble in common organic media, and give on hydrolysis the tribromohydroxydiphenylamine described by Smith and Orton (*loc. cit.*), this synthesis providing the further evidence required to establish it as *2 : 2′ : 4′-tribromo-4-hydroxydiphenylamine*.

The low solubility of tribromoacyloxydiphenylamines necessitated the following procedure: Finely powdered tribromo-4-*p*-toluenesulphonyloxydiphenylamine was exposed to the vapour of bromine in the presence of anhydrous sodium phosphate or sodium borate, and after 20 hours the absorbed bromine was removed by evacuation. Extraction with boiling benzene gave a quantitative yield of white, prismatic crystals of the sparingly soluble *2 : 6 : 2′ : 4′ : 6′-pentabromo-4-p-toluenesulphonyloxydiphenylamine*, m. p. 210° (Found: Br, 54·1. $C_{19}H_{12}O_3NBr_5S$ requires Br, 54·5%).

The *hydroxy*-compound (yield, 60%) crystallised from ligroin containing 5% of benzene, or from 75% alcohol, in massive, brown prisms, m. p. 206—207° (Found: Br, 68·5. $C_{12}H_6ONBr_5$ requires Br, 69·0%). The *benzoyloxy*-derivative, prepared by benzoylation in pyridine, separated after 24 hours and was precipitated from benzene solution by light petroleum in white needles, m. p. 141—142° (Found: Br, 58·6. $C_{19}H_{10}O_2NBr_5$ requires Br, 58·5%).

2 : 6 : 2′ : 4′ : 6′-*Pentabromobenzoquinoneanil*, prepared by the chromic acid method, has m. p. 184—185° (Found: Br, 68·7. $C_{12}H_4ONBr_5$ requires Br, 69·2%). Fission gave *s*-tribromoaniline and 2 : 6-dibromobenzoquinone.

Pentabromo-4-hydroxydiphenylamine with bromine in acetic acid solution in the absence of an absorbent for hydrogen bromide, yielded heptabromohydroxydiphenylamine (Smith and Orton, *loc. cit.*), but in the presence of sodium acetate oxidation to the violet quinoneanil occurred. An attempt to sulphonylate the heptabromohydroxy-compound by the Schotten–Baumann method gave a *substance*, m. p. 188°, soluble in 5% alcoholic potash, which was neither the initial material nor the desired sulphonyloxy-compound (Found: Br, 70·4%).

All attempts to sulphonylate 2 : 5 : 2′ : 4′-tetrabromo- and 2 : 3 : 5 : 2′ : 4′-pentabromo-4-hydroxydiphenylamine (Smith and Orton, *loc. cit.*) by the Schotten–Baumann procedure and the various modifications of Einhorn's method (compare Fischer and Pfaehler, *Ber.*, 1920, **53**, 1642; Ohle, *Ber.*, 1924, **57**, 409; Ohle and Dickhäuser, *Ber.*, 1925, **58**, 2593) failed.

In general, the sulphonyloxy-compounds are brominated more smoothly than the benzoyloxy-compounds, but the failure to sulphonylate the two hydroxy-compounds above led us to investigate the effect of bromine on the corresponding benzoyloxydiphenylamines. Although two positions ortho to the powerfully directing imino-group are present in 2 : 5 : 2′ : 4′-tetrabromo-4-benzoyloxydiphenylamine, this substance brominates too slowly to permit isolation of higher derivatives. Prolonged refluxing with bromine in carbon tetrachloride solution is followed by recovery of initial material. More drastic conditions such as the gaseous bromine–sodium phosphate method, or in chloroform in the presence of ferric chloride, lead to complete disruption of the molecule. Somewhat similar results followed from the work on 2 : 3 : 5 : 2′ : 4′-pentabromo-4-benzoyloxydiphenylamine, but gaseous bromine converted it into a viscous, dark liquid from which a small amount of heptabromobenzoyloxydiphenylamine was isolated.

Chlorobromo-compounds.

6 : 6′-*Dichloro*-2 : 2′ : 4′-*tribromo*-4-p-*toluenesulphonyloxy-* and -4-*benzoyloxy-diphenylamines.*—Because of low solubility, the tribromo-4-acyloxydiphenylamines were chlorinated in suspension in acetic acid solutions of dichloramine T (100% excess); after 18 hours, 2 equivalents of chlorine had disappeared, a quantitative yield of pentahalogenated derivative having separated.

The *sulphonyloxy*-compound melted, after crystallisation from petroleum, at 185° (Found: * Hals., 131·2; AgCl, 111·6. $C_{19}H_{12}O_3NCl_2Br_3S$ requires Hals., 131·9; AgCl, 111·3). The *benzoyloxy*-compound, after crystallisation from acetic acid, melted at 153° (Found: Hals., 140·9; AgCl, 119. $C_{19}H_{10}O_2NCl_2Br_3$ requires Hals., 143; AgCl, 120·6). Both esters are very sparingly soluble in all solvents. Hydrolysis of these gave the *hydroxy*-compound in small, brown prisms which, after twice crystallising from petroleum, melted at 166° (Found: Hals., 171·6; AgCl, 145·1. $C_{12}H_6ONCl_2Br_3$ requires Hals., 173·1; AgCl, 146·1).

6 : 6′-*Dichloro*-2 : 2′ : 4′-*tribromobenzoquinoneanil*, obtained by the chromic acid method, crystallised from acetic acid in deep purple, irregular prisms, m. p. 150° (Found: Hals., 173·1; AgCl, 147·8. $C_{12}H_4ONCl_2Br_3$ requires Hals., 174·0; AgCl, 146·6). By careful dilution of its solution in concentrated sulphuric acid, 2-chloro-4 : 6-dibromoaniline was obtained.

2 : 2′ : 4′-*Trichloro*-6 : 6′-*dibromo*-4-p-*toluenesulphonyloxydiphenylamine.*—Trichlorosulphonyloxydiphenylamine was brominated by the bromine vapour–sodium borate (phosphate) method. After crystallisation from benzene, chloroform, or petroleum, the product melted at 174°. Yield, quantitative (Found: Hals., 133·5; AgCl, 120·1. $C_{19}H_{12}O_3NCl_3Br_2S$ requires Hals., 134·3; AgCl, 119·5). The *benzoyloxy*-compound, prepared similarly, formed a sticky magma, which was suspended in acetic acid and freed from bromine by passage of sulphur dioxide. On warming, the material dissolved, and then separated in colourless prisms, m. p. 134° (Found: Hals., 149·6; AgCl, 133·8. $C_{19}H_{10}ONCl_3Br_2$ requires Hals., 146·5; AgCl, 130·8). The *hydroxy*-compound, after repeated crystallisation from 75% acetic acid, formed irregular prisms, m. p. 180°, readily soluble in all other organic solvents (Found: Hals., 176·5; AgCl, 157·8. $C_{12}H_6ONCl_3Br_2$ requires Hals., 180·5; AgCl, 160·9).

* For the Carius estimation of some of the substances here described, prolonged heating at 300° was required. In such cases, Robertson's method (J., 1915, **107**, 902) frequently proved of service. For the analysis of the chlorobromo-compounds, the mixture of silver halides (the weight of which, obtained from 100 parts of the substance, is denoted by "Hals.") obtained was usually converted into silver chloride by warming in a current of chlorine.

By the chromic acid method 2 : 2′ : 4′-*trichloro*-6 : 6′-*dibromobenzoquinoneanil* was obtained in massive, black prisms, m. p. 170° after crystallisation from chloroform (Found: Hals., 181·8; AgCl, 162·5. $C_{12}H_4ONCl_3Br_2$ requires Hals., 181·4; AgCl, 161·6). The fission of this quinoneanil requires care: a solution of 0·25 g. in 25 c.c. of concentrated sulphuric acid was slowly diluted with water to 20%. A small quantity of solid (unexamined) separated, and ether extraction then removed 2 : 4-dichloro-6-bromoaniline, m. p. 78° (acetyl derivative, m. p. 217°). Chattaway and Orton (J., 1901, 79, 816) give m. p. 83° and 218°, respectively.

2 : 2′ : 4′-*Trichloro*-5-*bromo*-4-*hydroxydiphenylamine*.—Trichlorohydroxydiphenylamine in acetic acid solution containing sodium acetate was oxidised by bromine, giving quinhydrone-like complexes, but their formation was avoided when 1·85 c.c. of bromine in 25 c.c. of chloroform were added to 10 g. of the amine in 100 c.c. of boiling chloroform during 1 hour; evolution of hydrogen bromide ceased after 2·5 hours. The solution, concentrated to 25—30 c.c., deposited matted needles which, after crystallisation from petroleum, melted at 127—128° (yield, 5·9 g.); a further 2 g. were recovered from the mother-liquor (combined yields, 60%). The compound is easily soluble in aqueous caustic soda (Found: Hals., 165·0; AgCl, 152·8. $C_{12}H_7ONCl_3Br$ requires Hals., 167·4; AgCl, 155·3). The *benzoyloxy*-compound separated from pyridine; m. p. 186° (Found: Hals., 129·4; AgCl, 120·0. $C_{19}H_{11}O_2NCl_3Br$ requires Hals., 131·2; AgCl, 121·7).

When the above hydroxy-compound was sulphonylated in the usual way, and the reaction product kept for 2 hours in a freezing-mixture, a red, crystalline solid separated. Following washing with water and with light petroleum, crystallisation from slightly diluted acetic acid gave colourless prisms of 2 : 2′ : 4′-*trichloro*-5-*bromo*-4-*sulphonyloxydiphenylamine*, m. p. 114° (Found: Hals., 117·9; AgCl, 109·5. $C_{19}H_{13}O_3NCl_3BrS$ requires Hals., 119·0; AgCl, 110·1).

2 : 2′ : 4′-*Trichloro*-5-*bromobenzoquinoneanil* (mercuric oxide method) crystallised from benzene or petroleum, or a mixture of the two, in hemispherical nodules of red, spear-shaped needles, m. p. 115°. Fission by solution in 45 volumes of concentrated sulphuric acid and slow dilution to 25% strength, followed by steam distillation, gave a yellow quinone, m. p. 172°, reduction of which by sulphur dioxide in aqueous-alcoholic solution gave a colourless quinol, m. p. 169° (2-chloro-5-bromobenzoquinone and 2-chloro-5-bromoquinol both melt at 172°). Neutralisation of the acid liquor, followed by distillation in steam, gave 2 : 4-dichloroaniline, m. p. 61° (acetyl derivative, m. p. 145°).

2 : 2′ : 4′-*Trichloro*-5 : 6′-*dibromo*-4-*hydroxydiphenylamine*, prepared

by refluxing trichlorobromohydroxydiphenylamine (10 g.) and bromine (1 mol.) in 80 c.c. of chloroform for 90 minutes, separated, on cooling, in white needles, m. p. 189° after two crystallisations from chloroform (Found: Hals., 176·9; AgCl, 160·5. $C_{12}H_6ONCl_3Br_2$ requires Hals., 180·5; AgCl, 160·9). Fractions obtained from the chloroform mother-liquor appeared to contain isomerides. Attempts to sulphonylate and benzoylate this substance failed.

2 : 2′ : 4′-*Trichloro*-5 : 6′-*dibromobenzoquinoneanil* (chromic acid method) formed small, vermilion, scintillating needles, m. p. 133° (Found: Hals., 177·7; AgCl, 159·1. $C_{12}H_4ONCl_3Br_2$ requires Hals., 181·4; AgCl, 161·4). Fission gave golden-yellow plates, m. p. 165° (2-chloro-5-bromobenzoquinone melts at 172°), and on dilution to 20% strength 2 : 4-dichloro-6-bromoaniline was precipitated.

2 : 2′ : 4′-*Trichloro*-3 : 5 : 6 : 6′-*tetrabromo*-4-*hydroxydiphenylamine*.—To a solution of 4 g. of trichlorohydroxydiphenylamine in 40 c.c. of chloroform boiling under reflux, 2·8 c.c. (4 mols.) of bromine in the same solvent were slowly added; hydrogen bromide was at first rapidly evolved. The mixture was then transferred to a silica flask, with excess of bromine, and exposed to sunlight for 3½ days, the solid that had separated after 12 hours being redissolved by gentle warming. The large, thin laminæ (3·9 g.) which separated were broken up, and freed from bromine and chloroform over charcoal and potash in a vacuum; m. p. 160°. Evaporation of the mother-liquor yielded a further 3·5 g. (combined yield, 89%) (Found: Hals., 194·5; AgCl, 165·1. $C_{12}H_4ONCl_3Br_4$ requires Hals., 195·7; AgCl, 166·2). The *benzoyloxy*-compound crystallised from chloroform–acetic acid in small, elongated prisms, m. p. 163° (Found: Hals., 169·8. $C_{19}H_8O_2NCl_3Br_4$ requires Hals., 169·7). Attempts to sulphonylate the hydroxy-compound failed.

2 : 2′ : 4′-*Trichloro*-3 : 5 : 6 : 6′-*tetrabromobenzoquinoneanil* (chromic acid method) crystallised from acetic acid in slender, indigo needles, m. p. 136°. Fission and dilution gave a very sparingly soluble substance, m. p. 294°, and 2 : 4-dichloro-6-bromoaniline. The literature notes the insolubility of chlorotribromoquinone and records two values for its m. p., *viz.*, 292° and 303°.

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UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

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CCCLXXXIII.—*Substitution Products of 4-Hydroxybenzophenone and of its Methyl Ether.*

By WILLIAM BLAKEY, WALTER IDRIS JONES, and HAROLD ARCHIBALD SCARBOROUGH.

THE orientation of substituents in the benzophenone series has been investigated in but few cases, *e.g.*, the introduction of bromine (Kottenhahn, *Annalen*, 1891, **264**, 170; Kunkel, *Ber.*, 1904, **37**, 3485), the direct nitration of benzophenone and of the isomeric mononitrobenzophenones (Staedel, *Annalen*, 1878, **194**, 347; 1883, **218**, 344; 1895, **283**, 164), and the introduction of a nitro-group into certain 4-halogenobenzophenones (Montagne, *Ber.*, 1916, **49**, 2262), and it was found that the first substituent entered the unsubstituted nucleus, usually with the production of the three possible isomerides.

The nitration of 4-methylbenzophenone gave derivatives the structure of which seems to be uncertain (Zincke, *Ber.*, 1872, **5**, 685; 1874, **7**, 983; Limpricht, *Annalen*, 1895, **286**, 324).

These results and those observed in the diphenyl series show marked similarities, and it therefore seemed of interest to consider the substitution products of 4-hydroxybenzophenone and of its methyl ether.

The direct chlorination of 4-hydroxybenzophenone in acetic acid solution gave 3 : 5-*dichloro*-4-*hydroxybenzophenone*; under all the conditions tried, the same product was obtained.

The reaction of 4-hydroxybenzophenone with bromine could be regulated, and 3-bromo- and 3 : 5-dibromo-4-hydroxybenzophenone were obtained when the ketone, dissolved in acetic acid, was treated with the appropriate quantity of bromine. The same dibromo-derivative was obtained when the ketone was shaken with an aqueous bromine solution or treated in alkaline solution with bromine.

The iodination of 4-hydroxybenzophenone in alkaline solution yielded the 3-*iodo*-derivative; treatment with iodine monochloride in acetic acid solution gave 3 : 5-*di-iodo*-4-*hydroxybenzophenone*.

A single nitro-group was introduced into 4-hydroxybenzophenone by treating the ketone with nitric acid in glacial acetic acid solution at 50° or by merely dissolving it in cold nitric acid. Solution in nitric acid at 40° gave 3 : 5-dinitro-4-hydroxybenzophenone. Attempts to obtain higher substitution products seemed to result in partial oxidation.

The direct chlorination of the methyl ether could be controlled and 3-*chloro*- and 3 : 5-*dichloro*-4-*methoxybenzophenone* were isolated.

On bromination of the methyl ether, 3-*bromo*-4-*methoxybenzo-*

phenone was obtained under all conditions which did not involve a demethylation. In contrast to this, the chlorination of the monobromo-derivative proceeded smoothly and 3-*chloro*-5-*bromo*-4-*methoxybenzophenone* was obtained.

The introduction of one atom of iodine was effected with iodine monochloride, and higher iodination products than 3-iodo-4-methoxybenzophenone could not be obtained.

The formation of 3-*nitro*-4-*methoxybenzophenone* took place when the methoxybenzophenone was dissolved in fuming nitric acid. Nitration in a mixture of sulphuric and acetic acids yielded a mixture of dinitro-compounds; the formation of 3 : 3′-*dinitro*-4-*methoxybenzophenone* has been definitely established. A second isomeride is most probably 2′ : 3-dinitro-4-methoxybenzophenone, but this structure is based on a process of elimination of probable products. In addition to these isomerides there was a residue which after repeated crystallisations still seemed to be a mixture.

Trinitration products were obtained when nitration was effected in concentrated sulphuric acid solution. The formation of 3 : 3′ : 5 *trinitro*-4-*methoxybenzophenone* has been definitely established; an isomeride is shown to have two nitro-groups in the 3 : 5-positions and it is suggested that the third nitro-group is in the 2′-position. After the separation of the two pure products, a residue was obtained which could not be further purified.

The most suitable methods for the determination of the structure of the substitution products were : (*a*) oximation and conversion of the oximes into anilides. This procedure was found satisfactory provided not more than one nitro-group was present in the molecule; considerable difficulty was experienced in effecting the oximation of dinitro-derivatives, and the product could not be purified easily. (*b*) Synthesis of the substituted ketone by the Friedel–Crafts reaction was effective in the case of certain of the nitro-derivatives.

Oxidation to a substituted benzoic acid was not very satisfactory, as it was difficult to avoid complete oxidation of the molecule.

A survey of the results obtained shows that in 4-hydroxybenzophenone each ortho-position with respect to the hydroxyl group may be substituted with ease, irrespective of the nature of the substituting groups. Substitution in the opposite nucleus could not be effected before the 3 : 5-positions were filled.

The methyl ether behaves somewhat differently, in that one position only in the ortho-relationship to the methoxyl group is usually substituted. Chlorine behaves abnormally, in that both positions may be substituted by this reagent. On nitration, a second substituent enters the unsubstituted nucleus.

A comparison of these results with those obtained in the diphenyl

series shows that in each case the presence of a hydroxyl group promotes substitution in all vacant positions in the ortho-para relationship to this group; the presence of such groups as the halogens or the nitro-group inhibits substitution in the same nucleus.

The conversion of the hydroxyl group into the methoxyl group reduces the directive power, and although the first substituent enters in an ortho-position to this group, the second entering group usually goes into the opposite nucleus.

EXPERIMENTAL.

4-Methoxybenzophenone was prepared from anisole and benzoyl chloride by Gattermann's method (*Ber.*, 1890, **23**, 1204).

4-*Hydroxybenzophenone.*—The hydrolysis of all the methyl ethers was effected as follows: 5 G. of the ether and 20 c.c. of 48% hydrobromic acid were dissolved in acetic acid and refluxed for about 12 hours. Part of the acetic acid was then removed, and the residue poured into water. The acid was neutralised with ammonia, the product taken up in ether, and the hydroxy-ketone shaken out with a 10% solution of sodium hydroxide and reprecipitated with sulphuric acid. 4-Hydroxybenzophenone separated from dilute methyl alcohol in prisms, m. p. 135°.

4-Acetoxybenzophenone was prepared by acetylation in pyridine solution. It crystallised from dilute methyl alcohol in needles, m. p. 81° (Found: C, 74·8; H, 5·1. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%).

3-*Chloro*-4-*methoxybenzophenone* was obtained when 4-methoxybenzophenone was treated with chlorine (slightly less than 1 mol.) in a cold solution of acetic acid. It separated from methyl alcohol in prisms, m. p. 98° (Found: Cl, 14·5. $C_{14}H_{11}O_2Cl$ requires Cl, 14·4%). On further chlorination in acetic acid solution, 3 : 5-dichloro-4-methoxybenzophenone (m. p. 74°) was obtained. The mono-derivative must therefore have been substituted in the 3-position.

3 : 5-*Dichloro*-4-*methoxybenzophenone.*—Into a solution of 10 g. of 4-methoxybenzophenone and 10 g. of fused sodium acetate in glacial acetic acid chlorine was passed until the gain in weight was 7 g. After some hours, the solution was poured into water. The product crystallised from alcohol in colourless needles, m. p. 74°. The same product was obtained by chlorination of the molten ketone in the presence of iodine or by chlorination in boiling carbon tetrachloride solution (Found: Cl, 25·2. $C_{14}H_{10}O_2Cl_2$ requires Cl, 25·3%).

The α-*oxime* was prepared by adding 10 g. of potassium hydroxide and 4·5 g. of hydroxylamine hydrochloride, each dissolved in the minimum quantity of water, to 6 g. of the dichloro-ketone dissolved in 100 c.c. of alcohol. The mixture was refluxed for 6 hours, the

alcohol in part removed, and the residue poured into water and neutralised with dilute hydrochloric acid. The oxime separated from alcohol in needles, m. p. 146° (Found: Cl, 23·9. $C_{14}H_{11}O_2NCl_2$ requires Cl, 24·0%).

3 : 5-*Dichloro*-4-*methoxybenzanilide*.—4 G. of the oxime, in dry ethereal solution, were treated with 7·5 g. of phosphorus pentachloride. After 12 hours, water was cautiously added and the ethereal layer was separated, washed, and dried. The *anilide*, after removal of the ether, crystallised from alcohol in pale yellow needles, m. p. 154° (Found: Cl, 23·95. $C_{14}H_{11}O_2NCl_2$ requires Cl, 24·0%).

On hydrolysis of the anilide (5 g.) with 20 c.c. of 10% hydrochloric acid for 6 hours at 140°, aniline and 3 : 5-*dichloroanisic acid* were obtained. 3 : 5-Dichloroanisic acid, prepared by the direct chlorination of anisic acid, crystallised from alcohol; m. p. 202° (Found: Cl, 32·05. $C_8H_6O_3Cl_2$ requires Cl, 32·1%). The acid was converted into the acid chloride, and the crude product added to a pyridine solution of aniline. The anilide thus obtained had m. p. 154°, alone or mixed with that prepared from the oxime.

3 : 5-*Dichloro*-4-*hydroxybenzophenone* was obtained from the methyl ether or by passing 5 g. of chlorine into a solution of 5 g. of 4-hydroxybenzophenone and 10 g. of sodium acetate in 100 c.c. of acetic acid and keeping the mixture for some hours. The product crystallised from methyl alcohol in needles, m. p. 148° (Found: Cl, 26·6. $C_{13}H_8O_2Cl_2$ requires Cl, 26·6%).

3-*Bromo*-4-*methoxybenzophenone*.—A solution of 5 g. of 4-methoxybenzophenone and 5 g. of sodium acetate in acetic acid was heated with 4·5 g. of bromine at 100° for 6 hours. The product separated from alcohol in needles, m. p. 94°. The same product was formed by bromination in the cold, in bright sunlight, or by heating together an intimate mixture of 5 g. of the ketone, 5 g. of sodium acetate, 4 g. of bromine, and 0·5 g. of pyridine (Found: Br, 27·5. $C_{14}H_{11}O_2Br$ requires Br, 27·5%).

Oximation of the ketone was carried out in the manner previously described. The α-*oxime* crystallised from alcohol in plates, m. p. 164° (Found: Br, 26·0. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). It was transformed into 3-*bromo*-4-*methoxybenzanilide*, which separated from alcohol in needles, m. p. 170° (Found: Br, 26·15. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). This anilide on hydrolysis yielded aniline and 3-bromoanisic acid and was prepared from the amine and the acid chloride.

The β-*oxime*, which remained in the mother-liquor, was precipitated with water. It separated from 30% aqueous alcohol in needles, m. p. 111·5° (Found: Br, 26·1. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). This oxime formed about 60% of the mixed oximes. On

transformation, *benzo-3-bromo-4-methoxyanilide* was obtained, which crystallised from alcohol in needles, m. p. 156° (Found : Br, 26·25. $C_{14}H_{12}O_2NBr$ requires Br, 26·15%). The anilide on hydrolysis gave 3-bromoanisidine (m. p. 56°) and was prepared from the amine and benzoyl chloride.

3-Bromo-4-hydroxybenzophenone was obtained by the hydrolysis of the methyl ether or by direct bromination of the ketone in acetic acid solution. It crystallised from alcohol in glistening needles, m. p. 183° (Found : Br, 28·75. Calc. for $C_{13}H_9O_2Br$: Br, 28·9%).

3-Chloro-5-bromo-4-methoxybenzophenone was obtained by leading chlorine into a glacial acetic acid solution of 5-bromo-4-methoxybenzophenone and fused sodium acetate, and precipitated after some hours by pouring the product into water. It separated from methyl alcohol in needles, m. p. 92° (Found : 0·1496 g. gave 0·1520 g. of silver halides. Calc. weight, 0·1523 g.). The structure assigned depends upon the fact that in no case has chlorine been introduced into the unsubstituted ring.

3 : 5-Dibromo-4-hydroxybenzophenone resulted from (*a*) direct bromination of the ketone in acetic acid solution (compare Hantzsch, *Ber.*, 1906, **39**, 3094; Kostanecki, *Ber.*, 1907, **40**, 3662); (*b*) the addition of a 5% solution of bromine in potassium bromide to the ketone dissolved in an excess of dilute potassium hydroxide, the temperature being kept below 5°; and (*c*) by shaking the ketone with bromine water. The product separated from alcohol in needles, m. p. 155°.

The same product was obtained when an intimate mixture of fused sodium acetate and 4-methoxybenzophenone was treated with bromine in a sealed tube at 140°.

3-Iodo-4-methoxybenzophenone.—10 G. of 4-methoxybenzophenone, dissolved in 100 c.c. of acetic acid, were treated with 12 g. of iodine monochloride. After 2 days, the mixture was poured into water, and the colour discharged with sulphur dioxide. The semi-solid mass crystallised from alcohol in needles, m. p. 81° (Found : I, 37·3. $C_{14}H_{11}O_2I$ requires I, 37·6%).

The *α-oxime* crystallised from alcohol in needles, m. p. 182° (Found : I, 35·9. $C_{14}H_{12}O_2NI$ requires I, 36·0%). On conversion of this oxime, *3-iodo-4-methoxybenzanilide* was obtained, which separated from alcohol in faintly yellow needles, m. p. 206° (Found : I, 35·9. $C_{14}H_{12}O_2NI$ requires I, 36·0%). The anilide on hydrolysis yielded aniline and 3-iodoanisic acid. The acid separated from alcohol in needles, m. p. 240° (Found : I, 45·55. Calc. for $C_8H_7O_3I$: I, 45·65%). A specimen of the acid was prepared from *p*-cresol for comparison.

The β-*oxime*, precipitated from the mother-liquor on addition of water, crystallised from 30% alcohol in needles, m. p. 135° (Found: I, 35·8%). This oxime, on conversion, yielded *benz*-3-*iodo*-4-*methoxyanilide*, which crystallised from alcohol in needles, m. p. 164° (Found: I, 35·9. $C_{14}H_{12}O_2NI$ requires I, 36·0%). On hydrolysis, the anilide yielded 3-iodoanisidine, which separated from alcohol–light petroleum in needles, m. p. 75° (Found: I, 51·1. Calc. for C_7H_8ONI: I, 51·0%).

The anilide was prepared from *o*-anisidine by the following stages: *o*-anisidine was converted into *o*-iodoanisole and nitrated in glacial acetic acid solution. The 2-iodo-4-nitroanisole thus obtained was reduced to the amine, which was treated with benzoyl chloride in pyridine.

3-*Iodo*-4-*hydroxybenzophenone* was obtained on the hydrolysis of the methyl ether or by treating an alkaline solution of 4-hydroxybenzophenone with a 5% solution of iodine in potassium iodide. The product separated from methyl alcohol in plates, m. p. 184° (Found: I, 39·05. $C_{13}H_9O_2I$ requires I, 39·2%).

3 : 5-*Di-iodo*-4-*hydroxybenzophenone*.—5 G. of the hydroxyketone together with 10 g. of sodium acetate were dissolved in 100 c.c. of acetic acid and treated with 9 g. of iodine monochloride. After 12 hours, the mixture was poured into water; the precipitate obtained crystallised from alcohol in feathery needles, m. p. 145° (Found: I, 57·6. $C_{13}H_8O_2I_2$ requires I, 57·7%).

3-*Nitro*-4-*methoxybenzophenone*.—A solution of 5 g. of 4-methoxybenzophenone in 50 c.c. of nitric acid (*d* 1·5) was kept for 12 hours, and then poured on ice; the semi-solid product crystallised from alcohol in yellow needles, m. p. 105° (Found: N, 5·5. $C_{14}H_{11}O_4N$ requires N, 5·45%).

An oxime was obtained when 17 g. of the nitro-compound dissolved in alcohol were treated with 14 g. of hydroxylamine hydrochloride and 11·5 g. of potassium hydroxide, each dissolved in the minimum quantity of water. A red coloration appeared in the solution and acetic acid was added until the colour became yellowish-green. After refluxing for 3 hours, the oxime was extracted in the usual way. The α-*oxime*, after repeated crystallisations from alcohol, separated in yellow plates, m. p. 179° (Found: N, 10·3. $C_{14}H_{12}O_4N_2$ requires N, 10·3%). On conversion the oxime yielded 3-*nitro*-4-*methoxybenzanilide*, which separated from alcohol in needles, m. p. 163° (Found: N, 10·3. $C_{14}H_{12}O_4N_2$ requires N, 10·3%). This anilide on hydrolysis gave 3-nitroanisic acid and aniline, and was prepared from the amine and the acid chloride.

3-Nitro-4-hydroxybenzophenone was obtained when (*a*) the methyl ether was hydrolysed, (*b*) 5 g. of 4-hydroxybenzophenone,

dissolved in a mixture of 100 c.c. of acetic acid and 20 c.c. of acetic anhydride, were treated with 1·5 c.c. of nitric acid (*d* 1·5), dissolved in 10 c.c. of acetic acid at 50—60°, and (*c*) a solution of 5 g. of the hydroxy-ketone in 100 c.c. of nitric acid (*d* 1·4) was kept at 0° for 2 hours. The product crystallised from methyl alcohol in plates, m. p. 94° (Borsche, *Ber.*, 1917, **50**, 1339, gives m. p. 120—121°) (Found: N, 5·7. Calc. for $C_{13}H_9O_4N$: N, 5·75%).

3 : 5-*Dinitro*-4-*methoxybenzophenone*.—5 G. of 4-chloro-3 : 5-dinitrobenzophenone (Ullmann, *Annalen*, 1909, **366**, 92), dissolved in dry methyl alcohol, were treated with a solution of 1 g. of sodium in methyl alcohol. After 12 hours, the product was precipitated by pouring the mixture into dilute hydrochloric acid. It separated from methyl alcohol in yellow needles, m. p. 105° (Found: C, 55·5; H, 3·4. $C_{14}H_{10}O_6N_2$ requires C, 55·6; H, 3·3%).

3 : 5-Dinitro-4-hydroxybenzophenone was prepared by Ullmann's method (*loc. cit.*) or by heating a solution of 5 g. of 4-hydroxybenzophenone in 100 c.c. of nitric acid (*d* 1·4) at 40° for 30 minutes. It crystallised from alcohol in yellow needles, m. p. 138° (Found: N, 9·85. Calc. for $C_{13}H_8O_6N_2$: N, 9·75%). The product of direct nitration did not appear to be a single substance, but no other pure compound was isolated.

3′-*Nitro*-4-*methoxybenzophenone*.—18 G. of *m*-nitrobenzoyl chloride and 10·5 g. of anisole, dissolved in 100 c.c. of carbon disulphide, were treated with 25 g. of aluminium chloride at room temperature, and the reaction completed on the water-bath. The product crystallised from alcohol in faintly yellow needles, m. p. 95° (Found: N, 5·5. $C_{14}H_{11}O_4N$ requires N, 5·45%). On hydrolysis, 3′-nitro-4-hydroxybenzophenone was obtained.

3 : 3′-*Dinitro*-4-*methoxybenzophenone*.—(*a*) A solution of 5 g. of 3′-nitro-4-methoxybenzophenone in 50 c.c. of nitric acid (*d* 1·5) was kept over-night. (*b*) 15 G. of 4-methoxybenzophenone, dissolved in a mixture of 60 c.c. each of acetic and sulphuric acids, were treated with 10 c.c. of nitric acid (*d* 1·5) below 10°; the product, which was a mixture of isomerides, was crystallised from acetic acid and then repeatedly from alcohol until a pure substance was obtained. (*c*) 5 G. of 3-nitro-4-methoxybenzophenone were nitrated, in solution in a mixture of sulphuric and acetic acids, with 2 c.c. of nitric acid (*d* 1·5). The yield was about 70% of the mixed nitration product.

It separated from alcohol in faintly yellow needles, m. p. 143° (Found: N, 9·3. $C_{14}H_{10}O_6N_2$ requires N, 9·2%).

3 : 3′-*Dinitro*-4-*hydroxybenzophenone* was obtained on demethylation. It separated from alcohol in faintly green prisms, m. p. 165° (Found: N, 9·8. $C_{13}H_8O_6N_2$ requires N, 9·75%).

The structure of these compounds follows from their method of preparation.

3 : 4′-*Dinitro*-4-*methoxybenzophenone*. — 4′-Nitro-4-methoxybenzophenone (Auwers, *Ber.*, 1903, **36**, 3891) was nitrated by dissolving it in nitric acid (*d* 1·5) and keeping the solution for 12 hours. The product separated from alcohol in small prisms, m. p. 174° (Found : N, 9·3. $C_{14}H_{10}O_6N_2$ requires N, 9·3%).

3 : 3′ : 5-*Trinitro*-4-*methoxybenzophenone*.—(*a*) A solution of 10 g. of 4-methoxybenzophenone in a mixture of equal volumes of sulphuric acid and nitric acid (*d* 1·5) was kept for 2 days. The product was a mixture of isomerides, which were separated by successive crystallisations from acetic acid, toluene, and acetic acid. (*b*) 3 : 5-Dinitro-4-methoxybenzophenone was nitrated under the same conditions and the isomerides were separated. (*c*) 3 : 3′-Dinitro-4-methoxybenzophenone on nitration gave an almost quantitative yield of the trinitro-compound. This isomeride formed about 65% of the crude nitration product and was sparingly soluble in toluene; it separated from acetic acid in prisms, m. p. 184° (Found : N, 12·05. $C_{14}H_9O_8N_3$ requires N, 12·1%). The structure assigned is based on three observations : (1) on prolonged oxidation with chromic anhydride in acetic acid solution, a small quantity of *m*-nitrobenzoic acid (m. p. 140°) was isolated, (2) on further nitration the two dinitro-4-methoxybenzophenones both yielded the same product, and (3) 3 : 3′-dinitro-4-methoxybenzophenone yielded one trinitro-compound only.

2′(?) : 3-*Dinitro*-4-*methoxybenzophenone* was obtained when the 3 : 3′-dinitro-compound had all been removed from the crude nitration product. It was crystallised from toluene and then from acetic acid, separating in needles, m. p. 125° (Found : N, 9·35. $C_{14}H_{10}O_6N_2$ requires N, 9·3%).

2′(?) : 3 : 5-*Trinitro*-4-*methoxybenzophenone* was obtained from the crude nitration products of 4-methoxybenzophenone and of 3 : 5-dinitro-4-methoxybenzophenone. It crystallised from toluene in glistening, light yellow plates, m. p. 142° (Found : N, 12·1. $C_{14}H_9O_8N_3$ requires N, 12·1%).

A definite structure cannot be assigned to these compounds, as all attempts to prepare a pure specimen of 2′-nitro-4-methoxybenzophenone failed. Three out of the four most probable dinitro-4-methoxybenzophenones, however, have been obtained in a state of purity and the dinitro-4-methoxybenzophenone, m. p. 125°, was not identical with any of these compounds.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE.

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CCCLXXXIV.—*The Temperature Effects of Mixing Non-aqueous Liquids.*

By WALTER MATTHEW MADGIN, JOHN BUTTERY PEEL, and HENRY VINCENT AIRD BRISCOE.

A GENERAL survey of the temperature changes occurring on mixing 628 pairs chosen from 37 non-aqueous liquids has shown that these changes are frequently of considerable magnitude (Madgin and Briscoe, *J. Soc. Chem. Ind.*, 1927, **46**, 107T). The present paper describes the further investigation of these changes in selected cases, undertaken in the expectation that some light might thereby be thrown upon the nature of liquids and liquid mixtures.

Relationship of Thermal Changes to the Polarity of the Constituent Liquids.—It has frequently been assumed (*e.g.*, Hildebrand, "Solubility," p. 85) that solubility is largely influenced by the relative polarity of the molecules concerned. The idea seems to be that a liquid composed of strongly polar molecules may easily dissolve another very polar liquid, but that the strong attraction between such polar molecules may hinder the interposition of non-polar molecules, and thus may even cause immiscibility with a non-polar liquid.

Detailed examination of the cases included in our original survey leads to the conclusion that there are many groups of liquids for which the relative values of the thermal effect of mixing differ widely from those to be expected from considerations of relative polarity. For example, hexane, benzene, and toluene are all very slightly polar by ordinary standards, and their polarities, as measured by the dielectric constant (*D.C.* = 1·85, 2·27, 2·34, respectively), increase slightly in the order named. In most cases the thermal effect of hexane with other liquids is more negative than that of benzene, which is again more negative than that of toluene. This is illustrated by the fact (Madgin and Briscoe, *loc. cit.*) that the number of positive heats of mixing given by hexane, benzene, and toluene, respectively, with the same set of other liquids is 0, 7, and 12. But in the case of the alcohols and carbon disulphide, benzene gives a greater decrease of temperature than either hexane or toluene; with alcohols, except methyl alcohol, toluene gives a greater negative effect than hexane; with methyl alcohol and carbon disulphide, hexane gives the greatest negative effect. These effects are not then in accordance with the order of dielectric constant.

Again, ethyl iodide generally gives a greater negative effect than ethyl bromide, which accords with the greater polarity of the former corresponding with the *D.C.* values: 9·4, 7·4; but exceptions

to this order occur in the heat effects with certain alcohols and carbon disulphide. Comparing the results of mixing ethylene dibromide, ethylene dichloride, chloroform, and bromoform with other liquids, it is noticeable that the chloro-compound generally gives the more positive heat of mixing, but exceptions occur in admixtures with ethyl and methyl iodides, with tetrachloroethane, and with aniline and carbon disulphide.

The doubt whether polarity can be assigned as a major cause of the temperature effects is intensified when we consider the cases in Table I and also that of water and ethyl alcohol (both having a

TABLE I.

	Dielectric constant.	Temperature change on mixing equal volumes.
Methyl acetate	7·1	
Ethyl iodide	7·4	− 5·1°
Ether	4·3	
Chloroform	5·1	+ 14·2
Acetone	21	
Chloroform	5·1	+ 12·65
Acetone	21	
Carbon disulphide	2·6	− 9·75
Acetone	21	
Ethyl alcohol	25	− 6·95

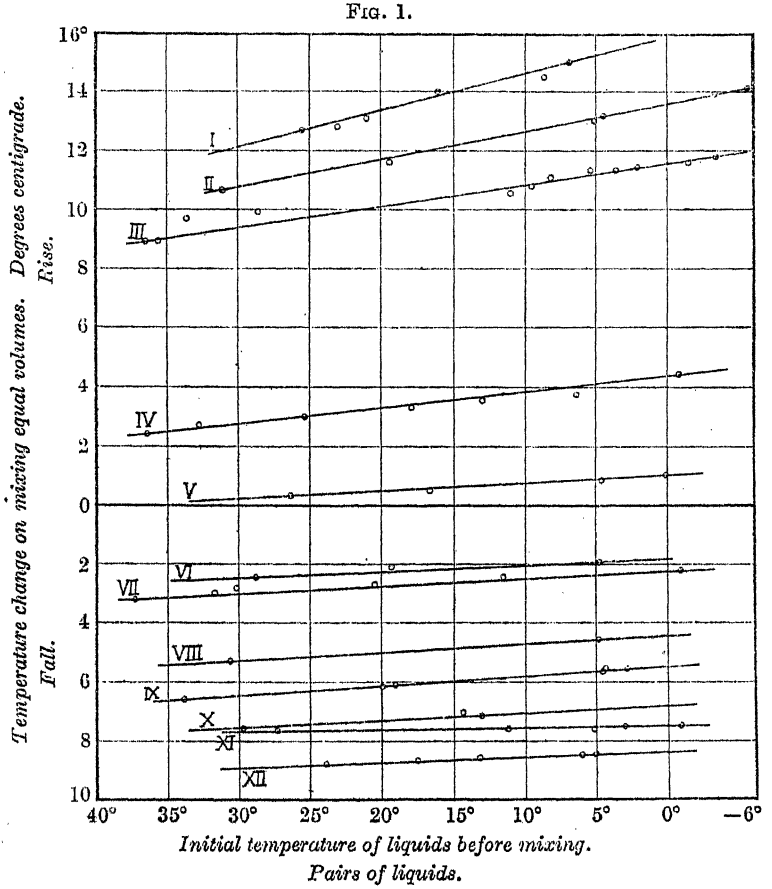
high *D.C.* and giving a rise of temperature on mixing), for it is apparent that either positive or negative heats of mixing may occur (*a*) with two liquids of small and similar *D.C.*, (*b*) with two liquids having respectively large and small *D.C.*'s, and (*c*) with two liquids both having large *D.C.*'s. Hence there seems to be no simple relationship between the heat of mixing and the polarity of the constituent molecules.

Effect of Variations of Initial Temperature on the Temperature Change on Mixing.—The literature contains very few references to investigations on the manner in which the temperature change on mixing varies with the initial temperature of the liquids mixed. Three isolated cases, two including water as one liquid, were investigated by Bussy and Buignet (*Ann. Chim. Phys.*, 1865, **4**, 5), and five cases, of which three included aniline as one liquid, have been investigated by Kremann and others (Kremann, *Monatsh.*, 1906, **27**, 91; Kremann and Pilch, *ibid.*, 1910, **31**, 203; Kremann, Meingast, and Guge, *ibid.*, 1914, **35**, 1235).

Therefore, as our general survey provided the necessary material for selection, it seemed well worth while to examine more widely the general trend of the thermal change with temperature for a series of mixtures ranging from those with large positive to those with large negative temperature changes on mixing. For this purpose, the apparatus used was a silvered Dewar tube (1″ diam. × 7″ deep

nternally) with narrow observation windows of the full height on opposite sides, provided near the mouth with three internal projections, on which rested the flange of a test-tube of such length that its thinly-blown closed end was about $\frac{1}{2}''$ from the bottom of the

FIG. 1.



Pairs of liquids.

I *o-Chlorophenol : aniline.* II *Chloroform : ether.* III *Chloroform : acetone.* IV *Chloroform : toluene.* V *Ether : toluene.* VI *Acetone : ether.* VII *Chloroform : hexane.* VIII *Ethyl alcohol : methyl acetate.* IX *Acetone : hexane.* X *Carbon disulphide : aniline.* XI *Carbon disulphide : ethyl oxalate.* XII *Carbon disulphide : acetone.*

Dewar tube. One liquid (10 c.c.) was placed in the Dewar tube, the other (10 c.c.) was within the test-tube : both were previously brought approximately to the desired temperature. In the test-tube were also a thermometer (− 20° to + 50° by 0·1°) and a pointed glass rod; when the tubes and liquids had attained the same constant temperature, the end of the test-tube was pierced by the

glass rod, the liquids were well mixed, and the temperature change was noted. To facilitate mixing, the denser of the two liquids was always put inside the test-tube. Twelve pairs of liquids were thus examined over a range of temperature; in most cases 6—8 observations were made, in some as many as 12. The whole of the observations are plotted in Fig. 1, and Table II gives for each pair of liquids (1) the temperature change from an initial temperature of 5°, (2) that from an initial temperature of 30°, and (3) the difference due to this change of 25° in the initial temperature.

TABLE II.

Pair of liquids.	1.	2.	3.	Pair of liquids.	1.	2.	3.
I	15·2	12·1	3·1	VII	−2·35	−3·0	0·65
II	13·1	10·8	2·3	VIII	−4·6	−5·3	0·7
III	11·15	9·4	1·75	IX	−5·65	−6·5	0·85
IV	4·1	2·8	1·3	X	−6·9	−7·6	0·7
V	0·9	0·2	0·7	XI	−7·6	−7·7	0·1
VI	−1·9	−2·4	0·5	XII	−8·5	−8·9	0·4

Inspection of the table shows at once that, whether the temperature change is positive or negative, its variation with initial temperature is always in the same direction; the temperature change is more positive (or less negative) the lower the initial temperature. On the other hand, the *magnitude* of the variation in temperature change obviously varies considerably throughout the series of mixtures, being generally greater the more positive (or less negative) the temperature change for a given initial temperature.

These observations receive a simple interpretation if, supposing each of the two liquids A and B to contain complex (A_x and B_y) and simple molecules, we assume that the latter, on admixture, may associate to form compound molecules, according to the scheme

$$\left.\begin{matrix} A_x \rightleftharpoons xA \\ B_y \rightleftharpoons yB \end{matrix}\right\} \rightleftharpoons zA_nB_m$$

and that the dissociations to the simple molecules are endothermic. The data here recorded are consistent with the view that alteration of the initial temperature changes the thermal effect in the A_nB_m equilibrium more than that in the A_x and B_y equilibria. This may occur through a change in the heat of reaction or through a shift of equilibrium, or for both of these reasons.

On entirely different grounds, Bramley (J., 1916, **109**, 43) reached a similar conclusion, which, therefore, whilst clearly needing further investigation, has a certain measure of probability.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research enabling the participation in

this work of one of us (J. B. P.), who has made a large number of the determinations of temperature change on which the present paper is based.

ARMSTRONG COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE. [*Received, April 30th*, 1927.]

CCCLXXXV.—*The Parachor and Chemical Constitution. Part VI. Some Cases of Supposed Ring-chain Tautomerism.*

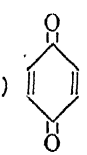
By FREDERICK BASIL GARNER and SAMUEL SUGDEN.

THE strictly additive character of the parachor sets obvious limits to its application to problems of chemical constitution, for a change in position of a radical or of a linkage in the molecule has no effect upon the value of this constant. If, however, two isomeric substances differ in structure by the replacement of a double bond by a ring, they should exhibit differences in parachor which will be greater the greater the number of atoms in the ring. The conversion of a double bond into a four-membered ring should give a decrease in the parachor of 11·6 units, whilst the corresponding figures for five- and six-membered rings are 14·7 and 17·1, respectively (see values for ring constants, Sugden and Wilkins, this vol., p. 142).

In this paper, the evidence of the parachor as to the structure of quinones, acid chlorides, and benzils is presented. Other substances in which similar structural changes have been postulated will be considered in later papers.

(1) *Quinones.*

Most of the reactions of *p*-quinones are represented by the formula (I), but the peroxide formula (II) has been suggested on chemical grounds by Graebe (*Annalen*, 1868, **146**, 1), whilst Hartley and Leonard (J., 1909, **95**, 34) and Haakh (*J. pr. Chem.*, 1910, **82**, 546), from a study of absorption spectra, and Binder (*Chem.-Ztg.*, 1921, **45**, 1114), from heats of combustion, also prefer formula (II).

(I.)  (II.) 

$>C(-COCl)-C(-COCl)<$ (III.)

$>C(-CCl_2-)C(=O)-CO-<$ (IV.)

We have measured the parachors of *p*-benzoquinone and tolu-

quinone with the following results, from which it is evident that the liquid substances contain little or none of the peroxide form.

TABLE I.

	[P], obs.	[P], calc. (diketone).	[P], calc. (peroxide).
p-Benzoquinone.....	236·8	236·1	219·0
Toluquinone	272·0	275·1	258·0

(2) *Acid Chlorides.*

The chlorides of dibasic acids would normally be assigned formula (III); in some reactions, however, these substances behave as if they possessed the structure (IV).

Auger (*Ann. Chim.*, 1891, **22**, 36), on chemical evidence, considered that succinyl chloride was a mixture of the two forms, the unsymmetrical chloride being in large excess. This view was criticised by Morrell (J., 1914, **105**, 1733), who maintained that this substance should be represented by the symmetrical formula. Ott (*Annalen*, 1912, **392**, 245) agreed with this, although his determinations of molecular volume seemed to indicate the existence of an equilibrium mixture of the two forms.

Phthalyl chloride offers a still more interesting example, for it has been obtained in two isomeric modifications melting at 15° and 88·5° (Ott, *loc. cit.*; Scheiber, *Ber.*, 1913, **46**, 2368; Csányi, *Monatsh.*, 1919, **40**, 81). Ott (*loc. cit.*) and Pfeiffer (*Ber.*, 1922, **55**, 413) have shown that the less stable high-melting modification has probably the unsymmetrical formula, whilst the low-melting form has the symmetrical structure.

We have prepared and examined succinyl chloride and the two forms of phthalyl chloride, with the results shown in Table II.

TABLE II.

Substance.	[P], obs.	[P], calc. (symmetrical).	[P], calc. (unsymmetrical).
Succinyl chloride	282·6	282·6	267·9
Phthalyl chloride, m. p. 13° ...	373·9	377·5	362·8
Phthalyl chloride, m. p. 88·5°	367·8	377·5	362·8

For succinyl chloride, the parachor shows clearly that the liquid has the symmetrical formula and cannot contain an appreciable amount of the unsymmetrical modification. With phthalyl chloride, a difference in the expected direction is found between the two isomerides, but the parachors are not in very good agreement with the predicted value in either case. This is probably to be explained by interconversion of the isomerides (compare Csányi, *loc. cit.*); the high-melting form is rapidly changed to the low-melting form at temperatures above its m. p. and shows a pro-

gressive change of density when kept at 90° for an hour. The figure given for this substance therefore represents a mixture containing a little of the low-melting isomeride (see p. 2881). We were unable to prepare the low-melting form with a m. p. higher than 13° (Csányi gives 15°), and this may also have contained a little of the other isomeride. In general, therefore, the parachor confirms the conclusions of Ott and Pfeiffer as to the structure of the two forms of this substance.

(3) *Benzils.*

Benzil and its derivatives may be formulated either as diketones (V) or as peroxides (VI). From its reactions and colour, benzil itself is usually assumed to have the ketonic structure. Certain



(V.) (VI.)

alkyloxy-derivatives of benzil are white, or very pale yellow in colour (Irvine, J., 1907, **91**, 536), and the view has been expressed, notably by Schönberg and his collaborators (Schönberg and Kraemer, *Ber.*, 1922, **55**, 1174; Schönberg and Malchow, *ibid.*, p. 3746; Schönberg and Bleyberg, *ibid.*, p. 3753), that these derivatives should be represented by the peroxide formula (VI). It should be noted, however, that on fusion these substances give yellow liquids which are supposed by Schönberg to contain an equilibrium mixture of the two forms.

We have prepared and measured 2 : 2′-dimethoxybenzil (Irvine's white benzil) with the results shown in Table III. It will be seen that the parachors found are in good agreement with the values calculated for the diketone formula in both cases, and show no indication of the presence of even a small proportion of the isomeride having the peroxide structure.

TABLE III.

Substance.	[*P*], obs.	[*P*], calc. (diketone).	[*P*], calc. (peroxide).
Benzil	480·8	476·0	464·4
2 : 2′-Dimethoxybenzil	596·8	594·0	582·4

EXPERIMENTAL.

In the course of this work new measurements have been made of the surface tension and density of *p*-benzoquinone, toluquinone, succinyl chloride, phthalyl chloride, benzil, and 2 : 2′-dimethoxybenzil. Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The constants for the bubbler used are: App. 14, $r_2 = 0{\cdot}177$ cm., $A = 0{\cdot}001020$. Densities were determined with the U-shaped pyknometer described previously (J., 1924, **125**,

1171), and are recorded in g. per c.c. All temperatures quoted are corrected by comparison with a standard thermometer with an N.P.L. certificate and are also corrected for exposed stem.

The tables are set out in the same manner as those given in earlier papers of this series and do not need further description. For all the substances studied in the present paper, d is very small and has been neglected.

p-*Benzoquinone*, $C_6H_4O_2$, $M = 108{\cdot}0$. A commercial specimen was purified by sublimation and melted at 115·5° (corr.). Some difficulty was encountered in the density determinations owing to the rapid sublimation of the substance into the cooler parts of the pyknometer; this sublimate was therefore removed and the tube reweighed after each volume determination. Densities determined: $D_4^{122°}$ 1·085, $D_4^{132°}$ 1·074, $D_4^{141·5}$ 1·064, $D_4^{160·5°}$ 1·044, whence $D_4^{t°} = 1{\cdot}214 - 0{\cdot}00106t$.

t.	P.	D.	ϕ.*	γ.	Parachor.
123·5°	2989	1·083	1·0435	31·81	236·8
139·5	2800	1·066	1·0456	29·86	236·9
154·0	2613	1·051	1·0482	27·94	236·2
167·5	2518	1·036	1·0493	26·96	237·4
					Mean 236·8

* A correction factor; see J., 1924, **125**, 31.

Toluquinone (2-methyl-1 : 4-benzoquinone), $C_7H_6O_2$, $M = 122{\cdot}1$, was recrystallised from dilute alcohol and melted sharply at 67° (corr.). In the density measurements, errors due to sublimation were avoided by adopting the procedure described for benzoquinone. Densities determined: $D_4^{75·5°}$ 1·081, $D_4^{89·5°}$ 1·069, $D_4^{103·5°}$ 1·056, $D_4^{114·5°}$ 1·045, $D_4^{127·5°}$ 1·034, whence $D_4^{t°} = 1{\cdot}152 - 0{\cdot}000926t$.

t.	P.	D.	ϕ.	γ.	Parachor.
76·5°	3191	1·081	1·0406	33·86	272·3
92·5	3010	1·066	1·0424	32·00	272·4
107·5	2836	1·052	1·0444	30·21	272·0
121·0	2687	1·040	1·0464	28·67	271·7
131·0	2586	1·031	1·0478	27·63	271·6
					Mean 272·0

Succinyl chloride, $C_4H_4O_2Cl_2$, $M = 155{\cdot}0$, was prepared by the action of phosphorus pentachloride on succinic acid and purified by repeated distillation under diminished pressure and freezing. The final product melted at 18·5° (corr.) and boiled at 95° (corr.)/20 mm. Densities determined: $D_4^{21°}$ 1·371, $D_4^{49°}$ 1·339, $D_4^{66°}$ 1·320, $D_4^{83·5°}$ 1·301, whence $D_4^{t°} = 1{\cdot}394 - 0{\cdot}00112t$.

t.	P.	D.	ϕ.	γ.	Parachor.
20·0°	3634	1·372	1·0452	38·75	281·8
49·5	3321	1·339	1·0483	35·50	282·5
65·0	3156	1·321	1·0502	33·81	283·0
79·5	2992	1·305	1·0522	32·21	282·9
					Mean 282·6

as-*Phthalyl chloride*, $C_8H_4O_2Cl_2$, $M = 203{\cdot}0$. Crude phthalyl chloride was prepared by the action of phosphorus pentachloride on phthalic anhydride and converted into the unsymmetrical form by heating with freshly prepared aluminium chloride (Ott, *loc. cit.*). The crude product was purified as described by Scheiber (*loc. cit.*) and Csányi (*loc. cit.*) by slow crystallisation from ligroin and mechanical separation of the prisms of the chloride from the needles of phthalic anhydride. After four crystallisations, a pure product was obtained, m. p. 88·5° (corr.).

This substance is transformed into the symmetrical modification at an appreciable rate even at temperatures just above the melting point. The stable form has a smaller density (1·327 at 90°), so that the transformation can be followed by the change in density. The following results were obtained when the pyknometer containing the unsymmetrical chloride was kept at 90° :

	First series.				Second series.			
Time (mins.) after melting	7	27	47	67	13	22	39	50
$D_4^{90°}$	1·351	1·349	1·347	1·346	1·350	1·348	1·347	1·346

At the end of the experiment the substance was cooled rapidly and its m. p. found to be 81—83°, so that a considerable transformation had taken place. The crystals in the pyknometer (about 2 g.) required about 30 minutes in the bath at 90° to melt completely; it is evident, therefore, that the highest density found (1·351) is still a little lower than that of the pure substance at this temperature; the parachor will therefore be a little too large. The two isomerides have almost the same surface tension at 90°; hence no change in this constant with time was found for the unsymmetrical chloride.

t.	*P*.	*D*.	ϕ.	γ.	Parachor.
90°	3358	1·351	1·0482	35·88	367·8

s-*Phthalyl chloride*, $C_8H_4O_2Cl_2$, $M = 203{\cdot}0$. This substance is difficult to free from phthalic anhydride except by crystallisation from ligroin in a cold room (compare Csányi, *loc. cit.*). As such a room was not available, we converted the purified unsymmetrical form into the symmetrical modification by heating at 150° for 1 hour. The product was fractionated under diminished pressure and the specimen used had b. p. 150° (corr.)/23 mm. and m. p. 13° (corr.). (Csányi gives 15°, but we were unable to obtain a product with this melting point after repeated freezings.) Densities determined: $D_4^{17·5°}$ 1·403, $D_4^{36·5°}$ 1·381, $D_4^{58°}$ 1·360, $D_4^{88·5°}$ 1·349, $D_4^{90°}$ 1·327, whence $D_4^t = 1{\cdot}420 - 0{\cdot}00104t$.

$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
15°	4169	1·404	1·0403	44·23	372·9
40	3867	1·378	1·0427	41·12	373·0
61	3692	1·357	1·0440	39·31	374·5
90	3390	1·327	1·0469	36·20	375·3
					Mean 373·9

Benzil, $C_{14}H_{10}O_2$, $M = 210·1$, was recrystallised from alcohol and melted sharply at 95° (corr.). Densities determined: $D_4^{103°}$ 1·084, $D_4^{118·5°}$ 1·071, $D_4^{134°}$ 1·059, $D_4^{151°}$ 1·047, $D_4^{163·5°}$ 1·037, whence $D_4^{t°} = 1·161 - 0·00076t$.

$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
103°	3573	1·083	1·0363	37·78	481·0
118·5	3415	1·071	1·0376	36·13	481·0
132	3289	1·061	1·0387	34·84	481·1
149	3125	1·048	1·0402	33·16	481·1
162	2984	1·039	1·0417	31·70	480·0
					Mean 480·8

2 : 2′-*Dimethoxybenzil*, $C_{16}H_{14}O_4$, $M = 270·2$. *o*-Methoxybenzaldehyde was first prepared by the careful methylation of salicylaldehyde with methyl sulphate: The aldehyde (1 mol.) and methyl sulphate (2 mols.) were mixed and mechanically stirred while caustic soda (5 mols.), dissolved in its own weight of water, was slowly added. The reaction vessel was well cooled and the addition of caustic soda stopped for a time when half of it had been added, the mixture having become a stiff cream; the addition of the remaining caustic soda caused the evolution of considerable heat, and the mixture became thinner. The stirring was continued for some hours after all the alkali had been added, and the mixture allowed to stand over-night. The crude product was separated, washed well with water, dissolved in ether, and the solution dried over calcium chloride. Finally, two distillations in a vacuum gave a pure product, b. p. 122°/20 mm., m. p. 37° (corr.).

The aldehyde was converted into the benzil, as described by Irvine (*loc. cit.*). The specimen used melted sharply at 130° (corr.). Densities determined: $D_4^{130°}$ 1·128, $D_4^{133°}$ 1·126, $D_4^{140°}$ 1·116, $D_4^{147·5°}$ 1·115, $D_4^{165°}$ 1·104, $D_4^{168·5°}$ 1·101, $D_4^{187°}$ 1·086, whence $D_4^{t°} = 1·217 - 0·00069t$.

$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
137·5°	3557	1·122	1·0378	37·64	596·5
155·5	3419	1·110	1·0389	36·22	597·2
178	3207	1·094	1·0409	34·04	596·6
					Mean 596·8

Summary.

(1) Measurements have been made of the surface tension and density of quinone, toluquinone, succinyl chloride, the two forms of phthalyl chloride, benzil, and 2 : 2′-dimethoxybenzil.

(2) The parachors calculated from these observations indicate that, except in the case of phthalyl chloride, these substances have the normal structure, and in the liquid state cannot contain more than a small amount of the isomeride in which a new ring is formed by tautomeric change.

(3) The parachors of the phthalyl chlorides indicate that the lower-melting form has the symmetrical structure, whilst the higher-melting form has the unsymmetrical structure.

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BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4. [*Received, October 15th*, 1927.]

CCCLXXXVI.—*The Chemical Nature of Precipitated Basic Cupric Carbonate.*

By JACK REGINALD IRONS HEPBURN.

THE author has previously studied (J., 1925, **127**, 1007) the mechanism of the changes which occur when precipitated cupric carbonate is kept in contact with the resulting solution. Special attention has now been directed towards the initial process which occurs on admixture of solutions of copper sulphate and sodium carbonate, the concentrations of which are systematically varied, with the object of gaining definite information as to the chemical nature of precipitated cupric carbonate, the composition of which is well known to depend on certain arbitrary factors, such as temperature of precipitation, relative proportions of admixed reagents, and time elapsing between precipitation and analysis. Serious analytical discrepancies have also been found to arise through inefficient mixing of the reacting solutions. In order to minimise such variations in the composition of the precipitate, a special mode of procedure was adopted in the present work.

If an excess of copper sulphate is used in the precipitation, and more especially if the sodium carbonate is added to the copper sulphate, the precipitate contains basic sulphate admixed with the basic carbonate. If the copper sulphate is added to excess of sodium carbonate, the precipitate consists of the basic carbonate, and the solution may contain carbonic acid, sodium hydrogen carbonate, or sodium carbonate, or mixtures of these compounds, according to the excess of sodium carbonate employed. On the other hand, with efficient stirring, and if the copper sulphate is

added to an equimolecular proportion of the sodium carbonate, the precipitate contains a relatively small percentage of basic sulphate, whilst the solution contains only carbonic acid and a small amount of dissolved copper.

The possibility of decomposition of the precipitate through subsequent drying or other further treatment was minimised by carrying out the analyses immediately after the reaction. The results thus obtained were reproducible, the effect of small temperature changes being unimportant.

In order to render the investigation as complete as possible, determinations have been made of copper and carbonic acid in the precipitate and in the solution after the reaction; of sodium carbonate remaining in solution, and adsorbed in the precipitate; and of adsorbed sulphate.

EXPERIMENTAL.

The solutions employed in the precipitations were all prepared by dilution from *M*-solutions. The cupric sulphate (A.R.) was used to standardise the sodium thiosulphate used in the subsequent copper estimations, and in the preparation of the *M*-cupric chloride solution. The cupric chloride employed was free from sulphate, but contained 22·9% of water; the solution was therefore made a little stronger than *M*, titrated against the standard thiosulphate solution, and diluted with the calculated amount of water. The *M*-sodium carbonate solution was standardised against the oxalic acid used in the carbon dioxide estimations, which had been previously standardised against pure sodium carbonate from bicarbonate. The oxalic acid was also employed in the estimations of sodium carbonate in solution. The potassium carbonate was prepared from bicarbonate and its titration against the oxalic acid confirmed the accuracy of the previous standardisation against sodium carbonate (Titration found: 27·65 c.c. Calc.: 27·67 c.c.). The barium hydroxide solution used in the estimations of carbon dioxide was preserved in an apparatus for titration in the absence of carbon dioxide. It was standardised against the oxalic acid.

The more dilute solutions were prepared in every case by dilution with water free from carbon dioxide and air. The volumes of the solutions employed were adjusted to yield a convenient quantity of precipitate, and varied from a minimum of 50 c.c. to a maximum of 1000 c.c. Equimolecular quantities of sodium carbonate and copper sulphate were used.

The experimental method adopted in the precipitations was similar to that described by Gröger (*Z. anorg. Chem.*, 1900, **24**, 127). The solution of copper sulphate was added in a fine stream

to that of sodium carbonate, violent mechanical stirring being employed throughout the addition. All the precipitations were carried out at room temperature (20°). The solution was filtered immediately after flocculation (5—10 minutes) through a Buchner funnel by means of the water-pump, and the precipitate was washed rapidly with cold water free from carbon dioxide and air.

Analysis.—(a) *Precipitate.* The moist precipitate was transferred to an apparatus for the estimation of carbon dioxide in carbonates (following the author's modification of Van Slyke's method, *Analyst*, 1926, **51**, 622), and analysed at once, loss of carbon dioxide from the precipitate through exposure to the air being thus eliminated. Copper was determined in the hydrochloric acid solution (remaining after the carbon dioxide estimation) by dilution, addition of sodium acetate in excess and of potassium iodide, and titration against standard sodium thiosulphate. Each determination was carried out in duplicate, except in Expts. 7 and 8 (Table I), where the amount of precipitate obtained was insufficient.

In the estimations of the adsorbed material in the precipitate, about 1 g. of the air-dried material was ignited to cupric oxide, extracted with boiling water, the filtrate concentrated, and titrated against 0·1*N*-oxalic acid for sodium carbonate (compare Applebey and Lane, J., 1918, **113**, 611). The remaining precipitate was dissolved in hydrochloric acid and added to the aqueous extract; the sulphate in the combined solution was then estimated as barium sulphate. (The solution was made up to 100 c.c. and 10 c.c. were titrated against the standard thiosulphate to determine the copper present, the remaining 90 c.c. being employed in the sulphate estimation.)

(b) *Filtrate.* A large volume of the filtrate was concentrated, whereby the copper was completely precipitated, with evolution of carbon dioxide; it was filtered off, dissolved in acetic acid, and titrated as usual. This filtrate was further concentrated and its sodium carbonate was estimated by titration in boiling solution against standard oxalic acid, phenolphthalein being used as indicator. Carbon dioxide in solution was determined by difference.

The results of the complete series of experiments (over a concentration range of *M* to 0·00625*M*) are given in Table I. The carbon dioxide content of the precipitate appears to vary continuously with the concentration of the reagents employed in the precipitation. The percentage of adsorbed copper sulphate at concentrations varying from 0·5*M* to 0·05*M* is small and erratic in nature; its variation is parallel to that in the concentration of the sodium carbonate remaining in solution (see Table V). The

TABLE I.

Expt. No.	Initial conc. (mols./litre).	Composition of precipitate. CO_2, g.	CuO, g.	Value of x in $2CuO,xCO_2$. x.	Mean.	Adsorbed $CuSO_4$, %.
1 a	1·00	0·1013	0·3480	1·052	1·044	—
b	,,	0·03704	0·1295	1·035		
2 a	0·50	0·09204	0·3146	1·058	1·052	0·16
b	,,	0·07145	0·2473	1·045		
3 a	0·25	0·05790	0·2200	0·952	0·945	1·84
b	,,	0·04290	0·1656	0·937		
4 a	0·10	0·0681	0·2845	0·906	0·902	2·25
b	,,	0·04508	0·1818	0·897		
5 a	0·05	0·02122	0·09572	0·802	0·798	2·21
b	,,	0·04296	0·1957	0·794		
6 a	0·025	0·03038	0·1476	0·744	0·737	—
b	,,	0·03833	0·1894	0·732		
7	0·0125	0·02004	0·1068	0·678	0·678	—
8	0·00625	0·02522	0·1463	0·623	0·623	—

percentage of adsorbed sodium carbonate is negligible. It seems probable that these small quantities of adsorbed material play no essential part in the reaction, and they have therefore been ignored in the following discussion.

The solubility of carbon dioxide in water at 20° corresponds with a concentration of 0·039*M* (Landolt–Börnstein, Tables, 5th Edn., 1923, 768). The solution resulting from admixture of approximately 0·25*M*-solutions of copper sulphate and sodium carbonate should therefore (from calculations based on the composition of the precipitate) be saturated with carbon dioxide; no effervescence occurred, however, on admixture of such solutions at 20°, whilst the effervescence was very slight in the case of 0·5*M*-solutions, and violent with *M*-solutions. The liquid in equilibrium with the precipitate from 0·5*M*-solutions appears, therefore, to be supersaturated with carbon dioxide, the concentration of carbon dioxide deduced from the composition of the precipitate being 0·119*M*. It was observed that the analytical figures for the precipitates from 0·5*M*-solutions and above were more variable than those for precipitates from more dilute solutions. This would be in accordance with the essential instability of supersaturated solutions and their sensitiveness towards small temperature changes. It will be noted particularly that the carbon dioxide content of the precipitates increases continuously until the concentration 0·5*M* is reached, but oscillates when this concentration is exceeded, suggesting a definite connexion between the concentrations of carbon dioxide in the liquid and the solid phases. It has accordingly been assumed that the concentration 0·119*M* for carbon dioxide in equilibrium with the precipitate was the maximum value possible.

All the experiments of Table I were carried out with copper sulphate and sodium carbonate. Precipitations with 0·5*M*- and 0·05*M*-cupric chloride and sodium carbonate, and with 0·5*M*- and 0·05*M*-copper sulphate and potassium carbonate, were also carried out, in order to ascertain whether the composition of the precipitated basic cupric carbonate was influenced to any extent by the acid and basic radicals associated with the cupric and carbonate ions (Table II). Although the results are not identical, and indicate some specific action of foreign ions, the composition of the precipitate approximates to the same value in each case.

TABLE II.

	Composition of precipitate.	
	Value of x in $2CuO,xCO_2$ for	
Precipitants used.	0·5*M*-Sols.	0·05*M*-Sols.
$CuSO_4$, Na_2CO_3	1·052	0·798
$CuCl_2$, Na_2CO_3	1·011	0·850
$CuSO_4$, K_2CO_3	0·999	0·833

Discussion.

The composition and the chemical nature of precipitated cupric carbonate have been investigated previously by several authors, and there is some divergency in the views expressed by them.

Gröger (*loc. cit.*) has studied the effect upon the carbon dioxide content of precipitated cupric carbonate, of steadily increasing the molecular proportion of sodium carbonate relative to copper sulphate. In his experiments, all the precipitations were carried out with *N*-solutions, and the concentration was not systematically varied as in the author's experiments, but the method of procedure was otherwise very similar. The products were air-dried before analysis. When the molecular ratio $Na_2CO_3 : CuSO_4$ was increased from 1·1 : 1 to 2 : 1, the carbon dioxide content was very much lowered (from $2CuO,1·012CO_2$ to $2CuO,0·802CO_2$). With a molecular ratio of 4 : 1 the carbon dioxide content was reduced still further ($2CuO,0·748CO_2$). The composition of the precipitate from approximately equimolecular quantities (1·1 : 1) of 0·5 *M*-solutions corresponds with $2CuO,1·012CO_2$, in close agreement with the author's result at this concentration, $2CuO,1·052CO_2$.

Employing sodium bicarbonate in place of the normal carbonate, Gröger found the carbon dioxide content of the precipitate to be increased—with approximately equimolecular solutions, the composition of the product corresponded with $2CuO,1·244CO_2$. He apparently regards the precipitated basic cupric carbonate as the decomposition product of the normal carbonate, for he states

(*loc. cit.*, p. 134) that it is not improbable that normal cupric carbonate is first formed and passes into the basic carbonate with loss of carbon dioxide. The high results for the carbon dioxide content of precipitates from sodium bicarbonate are held to agree with this view, by increasing the available carbon dioxide content of the reagent used, and so diminishing the extent of the decomposition. On the other hand, Gröger formulates the above product from bicarbonate as a definite compound, $8CuO,5CO_2,7H_2O$.

Pickering (J., 1909, **95**, 1409) attempted to ascertain the composition of precipitated basic cupric carbonate by adding sodium carbonate to a solution of copper sulphate sufficiently weak to ensure the retention of any carbon dioxide liberated (0·05% of copper). He found that alkalinity was attained when 1·61 mols. of sodium carbonate had been added per mol. of copper sulphate, and thence deduced the formula $5CuO,2CO_2$ (or $2CuO,0{\cdot}80CO_2$) for the precipitated substance. Pickering apparently assumes that the composition of the precipitate is independent of the concentration employed in the precipitation. This assumption has already been shown by the author to be untenable. Further, since the sodium carbonate was added to the copper sulphate, Pickering's compound undoubtedly contained basic sulphate.

Dunnicliff and Lal (J., 1918, **113**, 718) claimed to have prepared two new basic carbonates by precipitation from cupric sulphate–sodium carbonate mixtures of stated concentration, under standard conditions. Their method consisted in the addition of a cold 10% solution of sodium carbonate to a half-saturated solution of copper sulphate. The precipitate was kept for 24 hours, washed free from sulphate, and dried at 96° to constant weight. The mean of a number of analyses led to the formula $13CuO,5CO_2,9H_2O$. The second compound, prepared by adding a mixture of 5% sodium carbonate and 5% sodium bicarbonate solutions to the copper sulphate solution, corresponded to the formula $7CuO,2CO_2,5H_2O$.

The underlying idea in the experiments of Dunnicliff and Lal appears to be that any substance of constant composition which can be prepared under standard conditions is a definite compound, but, as judged by the author's results, these so-called compounds probably form points in a continuous curve; further, they appear to have no well-marked individuality or characteristics which distinguish them from other precipitates as definite compounds.

Mond and Heberlein (J., 1919, **115**, 908) have determined the composition of basic cupric carbonate precipitated from approximately 0·05*M*-solutions, under different conditions. The results indicate, contrary to those of Gröger, that the composition of the precipitated basic cupric carbonate was constant and independent

of the molecular proportion of cupric sulphate and sodium carbonate, in mixtures containing amounts in the proportion of 1 : 1 and lower. The molecular ratio in the precipitate was $CuO : CO_2 = 2{\cdot}26 : 1$ (or $2CuO,0{\cdot}885CO_2$). The amount of adsorbed material was relatively large, as is to be expected in the absence of an efficient stirrer. They concluded that no well-defined compound of copper is obtained by precipitation, the composition altering according to the conditions.

From theoretical considerations, there are a number of possibilities as to the chemical nature of the precipitated basic cupric carbonate. The simplest (Pickering; Dunnicliff and Lal) is to assume that a definite compound, or series of compounds, is formed. This view appears to be untenable in the light of the present experiments. A second view (Gröger) regards the substances as a mixture of the normal carbonate and the hydrated oxide. The various products are then regarded as due to the partial decomposition of the normal carbonate, and the variations of composition observed are attributed to greater or less decomposition, under given experimental conditions. It follows from this view, by the application of the mass-action equation $[CuO][CO_2]/[CuCO_3] = K$, that the concentration of the carbon dioxide in solution (or of carbonic acid), after precipitation, should possess a constant value, independent of the concentrations of the initial solutions employed in the precipitations; for, since both the normal cupric carbonate and the hydrated oxide may be regarded as very sparingly soluble in water, their active masses in solution would be constant.

It follows further, from this argument, that the amount of carbon dioxide retained in the precipitate at any particular initial concentration will diminish as the concentration of the precipitating solution is diminished, in order that this limiting concentration of carbon dioxide may be attained, after which no further loss of carbon dioxide from the precipitate should take place. Further, it appears that at a certain limiting value, *i.e.*, an initial concentration which will yield a concentration of carbon dioxide in the mother-liquor just equal to the equilibrium value, the precipitate should consist of the hydrated oxide only, and be free from carbon dioxide.

The experimental results for the concentration of carbon dioxide in the mother-liquor indicate, however, that this concentration diminishes steadily with the initial concentration of the reagents employed; the experimental result is therefore directly opposed to that derived from a consideration of the theoretical basis of Gröger's idea. A similar result follows if the basic cupric carbonate is regarded as the product of hydrolysis of the normal carbonate.

Free (*J. Amer. Chem. Soc.*, 1908, **30**, 1366) has suggested that the precipitated basic cupric carbonates might be regarded as solid solutions of carbonic acid with hydrated cupric oxide. This view does not appear to be very probable.

Certain basic salts produced by precipitation have been subjected to phase-rule studies (compare Britton, J., 1925, **127**, 2796), and the results have been held to be comparable with those obtained in initial precipitation processes. It appears to be a condition of such studies—more particularly those employing Schreinemakers's method of residues—that the liquid phase should be in equilibrium with a definite solid phase (or phases), *i.e.*, a well-characterised (probably crystalline) substance. In cases where a definite product is not obtained (*e.g.*, a colloidal substance, as obtained by Carter and Hartshorne, J., 1923, **123**, 2223, in their study of the system ferric oxide–phosphoric acid) the phase-rule method yields no definite result. Further, sufficient time must be allowed in phase-rule studies to enable a definite equilibrium to be reached. When such a state has been attained, the solid phase in equilibrium with the liquid is generally found to be crystalline (compare Carter and Hartshorne, *loc. cit.*).

It appears, therefore, that the initial product in a precipitation change must be distinguished from that obtained in a phase-rule study, or, in the particular case under investigation, that the initial precipitate is entirely different in nature from the stable basic carbonate, malachite, which is obtained under special conditions (compare J., 1925, **127**, 1007).

For the particular conditions maintained in the author's experiments, the final products of the precipitation at each concentration (neglecting small amounts of fortuitous impurities) consisted of a solid phase containing cupric oxide and a liquid phase containing carbon dioxide together with sodium sulphate. When the concentration of carbon dioxide in solution is plotted against the carbon dioxide content of the precipitate, Curve I (Fig. 1), is obtained. The carbon dioxide content, a, of the solid phase is evidently a continuous function of that in the liquid phase, c; further there is an exponential relation between these two magnitudes. When the logarithms of the two quantities are plotted, the points obtained lie, within the limits of experimental error, along a straight line (Curve II; Fig. 1). These results, therefore, are in accordance with the criteria usually applied to adsorption effects.

According to Freundlich ("Colloid and Capillary Chemistry," 1926, p. 172), the general form of the adsorption isotherm is represented by the equation

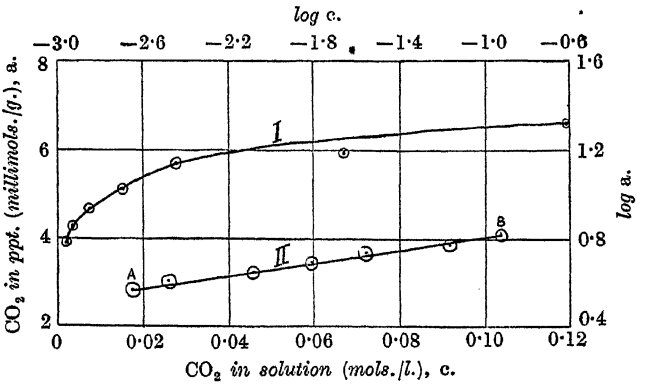
$$a = \alpha(c)^{1/n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $1/n$ has a value between 0·1 and 0·5, whilst the constant α may vary within wide limits. [The concentration c is given in mols. per litre, whilst the quantity a is calculated in millimols. per g. of adsorbent (anhydrous cupric oxide).] The value of $1/n$ was calculated to be 0·130 from the co-ordinates of the points A and B, both of which fell on the logarithmic line. From this value and the observed values of a and c, α was found to be 8·75, by substitution in (1). Hence

$$a = 8{\cdot}75c^{0{\cdot}130} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By use of this equation, the theoretical values for a have been calculated at the concentrations actually employed, and compared

FIG. 1.



For Curve I, use ordinary co-ordinates.
For Curve II, use logarithmic co-ordinates.

with the experimental figures (Table III, columns 2 and 3). The agreement appears to be satisfactory.

TABLE III.

Equil. conc. of CO_2 in soltn. (mols./l.).	CO_2 in precipitate (millimols. per g.). Found.	Calc.	Equil. conc. of CO_2 in soltn. (mols./l.).	CO_2 in precipitate (millimols. per g.). Found.	Calc.
0·119	6·61	(6·63)	0·00789	4·63	4·66
0·0668	5·94	6·15	0·00319	4·26	4·15
0·0275	5·67	5·48	0·00215	3·92	(3·94)
0·0150	5·01	5·07			

There is a marked parallelism between these results and those of Biltz (*Ber.*, 1904, **37**, 3138) for the adsorption of arsenious oxide by hydrated ferric oxide. Biltz's figures have been recalculated according to the adsorption equation

$$a = 6{\cdot}02c^{0{\cdot}200} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the values obtained are in Table IV.

TABLE IV.

Equil. conc. of As_2O_3 in soltn. (mols./l.).	As_2O_3 in precipitate (millimols. per g.). Found.	Calc.	Equil. conc. of As_2O_3 in soltn. (mols./l.).	As_2O_3 in precipitate (millimols. per g.). Found.	Calc.
0·0979	3·77	(3·77)	0·0125	2·51	2·51
0·0603	3·40	3·43	0·00699	2·32	2·23
0·0479	3·26	3·28	0·00427	2·21	2·02
0·0422	3·10	3·19	0·00270	1·90	1·85
0·0330	2·99	3·04	0·00114	1·59	1·55
0·0240	2·82	2·85	0·00025	1·15	(1·15)
0·0178	2·75	2·69			

TABLE V.

Conc. of original solution (mols./litre).	Equil. conc. of CO_2 (mols./litre).	Conc. of Cu in solution (mols./litre).	% Cu not pptd.	Conc. of Na_2CO_3 in solution (mols./litre).	% Na_2CO_3 not pptd.
1·00	—	0·0047	0·94	0·0030	0·60
0·50	0·119	0·0049	1·98	0·0007	0·28
0·25	0·0668	0·0036	2·9	0·0014	1·1
0·10	0·0275	0·0018	3·6	0·0009	1·8
0·050	0·0150	0·0011	4·4	0·00034	1·4
0·025	0·0079	0·00071	5·6	0·00031	2·5
0·0125	0·0032	0·00050	8·0	Trace	—
0·00625	0·0022	0·00026	8·6	,,	—

Further, the values for $1/n$ are within the limits laid down by Freundlich for typical adsorptions, but somewhat lower than the average (0·3—0·5), whilst the constant α is in both cases well within the range of values usual for such phenomena. A further parallelism appears in the nature of the adsorbed substance. The cases of adsorption from aqueous solution which have been investigated most thoroughly are those of the weak organic acids by charcoal, and in the present case the adsorbed substance is apparently carbonic acid, a weak acid the strength of which is of the same order of magnitude as those of the organic acids.

The precipitated cupric oxide appears to be present, when initially precipitated, in a very finely divided condition, as is indicated by the abnormally large solubility in the carbon dioxide in solution. Such a large effective surface would facilitate large and rapid adsorption.

The author therefore puts forward the view that the formation of precipitated cupric carbonate is due, not to dissociation of the normal carbonate, but to adsorption of un-ionised carbonic acid by hydrated cupric oxide in a very active state.

The fact that the composition of the basic cupric carbonate precipitated from 0·5*M*-solutions approximates to the formula $2CuO,CO_2$, independently of the particular salt of copper employed suggests that a definite compound is produced at this concentration. Further, this composition represents the maximum value for the

carbon dioxide content when the precipitations are carried out with sodium carbonate and copper sulphate. According to the views put forward by the author, however, the agreement of the analytical figures at this concentration with the formula for malachite is only a coincidence. The carbon dioxide content of the precipitate is conditioned by its concentration in the liquid phase, and the maximum value of this concentration is further limited by the solubility of carbon dioxide in water, which may, however, be affected by the formation of supersaturated solutions. If the solubility of carbon dioxide in water could be made to exceed this value, the carbon dioxide content of the precipitate would be expected to be higher. This prediction finds support in Gröger's results for precipitations with bicarbonate: in the presence of sodium bicarbonate the solubility of carbon dioxide is increased, and the concentration of un-ionised carbonic acid is further increased by the excess of bicarbonate ions, according to the relation $[H^{\cdot}][HCO_3']/[H_2CO_3] = K_1$. Actually, under these conditions the carbon dioxide content of the precipitate was increased.

The author has carried out a number of experiments with the object of approaching the equilibrium from the other side, *viz.*, from hydrated cupric oxide and aqueous solutions of carbon dioxide, but certain difficulties rendered it impossible to obtain definite results. Primarily, it was not found possible to prepare hydrated cupric oxide free from notable amounts of cupric sulphate, without the occurrence of blackening, due to traces of alkali. It is thought that more definite results might be obtained by the use of a more stable hydrogel, *e.g.*, hydrated ferric oxide.

The idea that certain basic salts might be adsorption compounds has recently been tentatively put forward by Britton (J., 1926, 125) to explain the fact that the thorium hydroxide precipitated from thorium nitrate by addition of potassium chromate contained large amounts of chromic anhydride, the presence of which was attributed to "a process akin to adsorption, in which the chemical tendencies of the weak acid and the weak base played an important part." Although no further experimental verification of this statement was adduced, the idea is analogous to that now suggested by the author.

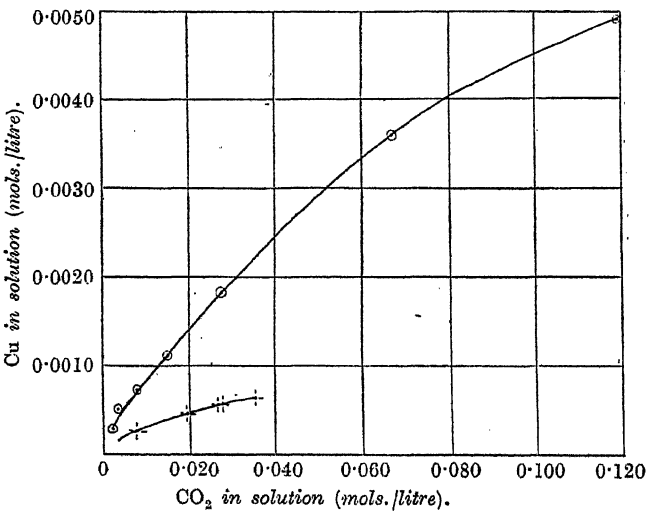
The Copper in Solution.

At every concentration at which the precipitation was carried out, it was found that a definite concentration of copper in solution was attained, after precipitation, dependent upon the concentration of carbon dioxide in the final solution. The relation between these two concentrations is represented by a smooth curve, shown in Fig. 2. The regularity of the results is striking, in view of the fact

that the carbon dioxide contents of the precipitates obtained at each concentration were widely divergent, the value of x in the formula $2CuO,xCO_2$ varying from 1·052 to 0·623; in spite of this, these precipitates behave in the same way as regards their solubility in aqueous solutions of carbon dioxide, which suggests that they are of very similar chemical nature. Such would be the case if each precipitate consisted of hydrated cupric oxide with variable quantities of adsorbed carbon dioxide.

Mond and Heberlein (*loc. cit.*) have determined the concentration of copper in the solution remaining after a precipitation from

FIG. 2.



⊙ *Author* (*see Table V*). ⊹ *Free.*

0·05*M*-solutions of cupric sulphate and sodium carbonate. They found this concentration to be 0·0032*M* (representing 8·0% of the total copper originally in solution), whereas the author's experiments at 0·05*M* gave 0·0011*M* (representing 4·42% of the original copper). Their corresponding concentrations of sodium carbonate remaining in the mother-liquor were also much higher than those found by the author. It is suggested that these high results are to be attributed to incomplete mixing owing to the lack of an efficient stirrer.

According to Mond and Heberlein, the dissolved copper is present in colloidal solution as the basic sulphate, and the sodium sulphate present in the solution may be removed by dialysis; they also state that the basic carbonate itself is not appreciably soluble in

water in the presence of carbon dioxide. In the author's opinion, these views are based upon insufficient experimental evidence, for the statement that the substance in solution is the basic sulphate appears to be founded upon one analysis of the precipitate formed after expelling carbon dioxide from the solution by boiling, whereby any carbon dioxide in the precipitate would also be removed. The black precipitate so produced contained $SO_3 : CuO = 1 : 4$.

The copper in solution is completely precipitated by boiling and expelling the carbon dioxide, the solution is colourless and not opalescent, and on exposure to air in an open vessel it loses carbon dioxide rapidly, with film formation of the basic carbonate on the surface. Under such conditions, it is difficult to understand how Mond and Heberlein were able to dialyse such a solution without decomposition and precipitation through loss of carbon dioxide.

Previous determinations of the solubility of basic cupric carbonate in aqueous solutions of carbon dioxide have been carried out by Free (*loc. cit.*). Precipitated basic cupric carbonate was agitated with a solution of carbon dioxide of known concentration, and the concentration of copper in solution was estimated after equilibrium had been attained. It was found that freshly precipitated basic cupric carbonate was more soluble in aqueous carbon dioxide solutions than the stable crystalline basic salt (malachite), and that the solubility of the freshly precipitated substance steadily decreased with time, finally reaching constancy at the value representing the solubility of malachite in the particular concentration of carbon dioxide. At the same time it was observed that the substance had been transformed into malachite.

The maximum value obtained by Free in any experiment was 107 parts of copper per million parts (or 0·00167 g.-atom per litre), in a solution of carbon dioxide containing 1200 parts per million. The author's result at this carbon dioxide concentration corresponds with 0·0018 g.-atom per litre. The agreement for freshly precipitated basic cupric carbonate is therefore satisfactory.

The author's results for the concentration of copper in solution are approximately three times as high as those obtained by Free for malachite (*e.g.*, for a solution containing 0·0275 mol. of CO_2 per litre, the concentration of Cu in solution was 0·0018 g.-atom per litre, whereas Free's result for a solution containing 0·0278 mol. of CO_2 per litre was 0·00054 g.-atom of Cu per litre). It is probable, therefore, that the freshly precipitated basic cupric carbonate is in a very finely divided condition, since below a certain limit of particle size the solubility of such precipitates is known to increase with the degree of dispersity. It may be observed, in this connexion, that Seyler (*Analyst*, 1908, **33**, 454) has attributed

the regularities found in Free's results to the formation of cupric bicarbonate in solution, and has attempted to show, by the application of ionic principles, that the solubility relationships are in accordance with this assumption.

Summary.

The effect of systematic variation in the concentration of the precipitants (copper sulphate and sodium carbonate) on the carbon dioxide content of precipitated basic cupric carbonate has been studied. The solutions employed were equimolecular, and the concentration ranged from M to $0{\cdot}00625M$. The results obtained indicate that the carbon dioxide content of the precipitate is a continuous function of the concentration of carbon dioxide in solution, and that these two magnitudes are capable of representation by a Freundlich adsorption equation. The view is therefore advanced that the formation of basic cupric carbonate is due to an adsorption process, the absorbent consisting of hydrated cupric oxide in a very active state, and the adsorbed material being un-ionised carbonic acid.

The author wishes to thank Dr. T. J. Drakeley for facilities provided during the course of this work.

NORTHERN POLYTECHNIC,
LONDON, N. 7.

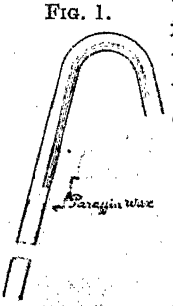
[*Received, October 3rd,* 1927.]

NOTES.

A Simple Form of Automatic Syphon. By DOUGLAS CREESE HARRISON.

THE syphon is made of glass tubing of diameter not greater than 5 mm. About eight capillaries of diameters varying between about ¼ mm. and 1 mm. and about 20 cm. long are drawn from the same tubing and placed inside the glass tube near one end. The tube is then heated not too strongly and bent to form the syphon, with the capillaries inside the bend and projecting about 7 cm. into the shorter limb of the syphon. The longer limb (which should extend well below the ends of the capillaries) is warmed and molten paraffin wax is drawn into it to within about 4 cm. of the ends of the capillaries. The wax is allowed to run down and the excess shaken out, so that, when cool, a thin, even layer remains on the inside of the tube. The wax serves to retain the drops of liquid drawn

FIG. 1.



through the capillaries by surface tension, until, within a few seconds, they have accumulated to form a column of liquid heavy enough to draw liquid over the bend of the large tube. The height to which the liquid can be raised in starting the syphon will depend, of course, on the surface tension of the liquid and the cross-section of the capillaries. It is advantageous to use a number of capillaries of various diameters, since the liquid will rise more rapidly and to a greater height in the smaller capillaries and, as the liquid begins to accumulate in the longer tube, the pull exerted by gravity will assist the syphoning of the liquid in the larger capillaries. In this way the flow will become faster and faster until the liquid is drawn over the bend and syphons in the large tube. The capillaries occupy only a small part of the tube and so allow a rapid flow of liquid through the syphon.—SHEFFIELD UNIVERSITY. [*Received, August 18th*, 1927.]

The Preparation of Triacetonamine Hydrate. By FRANCIS FRANCIS.

THE following method was devised some years ago, but was not described at the time, since it was desired to investigate the other products of the reaction and to increase materially the yield of the base.

Into a mixture of 2½ kg. of acetone and 800 g. of fused calcium chloride in a large round-bottom flask provided with an efficient condenser, ammonia is passed at intervals until the whole of the chloride has been converted into a liquid complex. After 3 days the product is gently boiled on a water-bath until the liquid calcium chloride–ammonia compound has decomposed and resolidified, ammonia being evolved. The dark, strongly smelling liquid is then decanted from the solid or pasty chloride, and distilled until a thermometer in the vapour registers 75°; the distillate consists chiefly of acetone. The residue is placed in a freezing mixture of ice and hydrochloric acid, and when the temperature has fallen to 1—2° an amount of water is added, with vigorous stirring, corresponding to a yield of 28% of triacetonamine calculated on the acetone used, *i.e.*, the amount taken less that distilled off. Triacetonamine hydrate separates in a crystalline condition as the temperature falls; after being pressed between filter-paper and recrystallised several times from undried ether, it is obtained in large, well-formed, slightly yellow crystals (yield, 20—26%, calculated on the acetone used).

The conversion of the hydrate into nitrosotriacetonamine is carried out in the usual manner and the yield is quantitative. The extreme ease with which this nitrosoamine is decomposed catalytic-

ally by alkalis, giving a nearly quantitative yield of phorone, renders this an elegant method for the preparation of this unsaturated ketone (J., 1912, **101**, 2358).—THE UNIVERSITY, BRISTOL. [*Received, September 15th*, 1927.]

7-Hydroxy-3-phenylcoumarin. By WILSON BAKER.

AN attempt was made to synthesise 3-phenylchromones (*iso*flavones; Baker and Robinson, J., 1925, **127**, 1981; 1926, 2713) by condensing ethyl α-formylphenylacetate with resorcinol or phloroglucinol in presence of phosphoric anhydride. By analogy with ethyl acetoacetate and its derivatives, chromones should be produced (see papers by Simonis and collaborators, *Ber.*, 1913, **46**, 2015; 1914, **47**, 692, 2229, etc.), but the first condensation gave only 7-hydroxy-3-phenylcoumarin, which has also been prepared (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 121; Bargellini, *Gazzetta*, 1927, **57**, 459) from resorcylaldehyde, sodium phenylacetate, and acetic anhydride.

Jacobson and Ghosh (J., 1915, **107**, 1057) and Ghosh (J., 1916, **109**, 114) describe the reactions between ethyl α-formylphenylacetate and resorcinol, in presence of acetic acid and zinc chloride, and between formylphenylacetonitrile and resorcinol in presence of phosphoryl chloride, and the isolation in both cases of a substance, m. p. 131°, described by them as 7-hydroxy-3-phenylchromone. Since such condensations are now known to give coumarins (Baker and Robinson, J., 1925, **127**, 1981; Baker, *ibid.*, p. 2349; Bargellini, *Gazzetta*, 1925, **55**, 945), and the substance, m. p. 131°, could not be identical with 7-hydroxy-3-phenylcoumarin, which melts at 207—208°, the experiments were repeated, with the result that both gave the same product, m. p. 207—208°, identical in all respects with 7-hydroxy-3-phenylcoumarin. The product, m. p. 131°, is, therefore, not the product of these condensations, and its description is doubtless due to confusion of specimens in the laboratory.

7-Hydroxy-3-phenylcoumarin.—Ethyl α-formylphenylacetate (15 g.), xylene (75 c.c.), and resorcinol (50 g.) were heated at 160° for 2 hours, phosphoric anhydride (50 g.) being gradually added. The product, boiled with water to expel the xylene, was converted into the acetyl derivative, which, after twice recrystallising from acetic acid (charcoal), separated in colourless, flat prisms, m. p. 184—185°. No trace of an *iso*flavone could be detected in the mother-liquors. Hydrolysis produced 7-hydroxy-3-phenylcoumarin, which separated from alcohol in prisms, m. p. 207—208°, containing alcohol of crystallisation. The methyl ether, prepared by the action of methyl sulphate, crystallised from alcohol in colourless, nacreous plates, m. p. 124° (Bargellini, *loc. cit.*, gives m. p. 118—120°) (Found:

C, 76·0; H, 4·6. Calc.: C, 76·2; H, 4·8%). These compounds give yellow solutions in concentrated sulphuric acid, which exhibit an intense bluish-green fluorescence.

Condensation of Ethyl α-Formylphenylacetate with Phloroglucinol.—The two substances (15 g. of each), treated as previously described, gave an *acetyl* derivative (0·6 g.) which crystallised from acetic acid in hair-like, colourless needles, m. p. 255—256° (Found: C, 73·7, 73·6, 73·7; H, 4·2, 3·8, 4·6%; *M*, by Rast's method, 434, 416). Hydrolysis with potassium carbonate in 50% alcohol gave a phenolic substance which crystallised from alcohol in pale yellow prisms, m. p. 308—310° (decomp.) (Found: C, 72·2; H, 4·5%). This compound of high molecular weight is not identical with the 5 : 7-dihydroxy-3-phenylcoumarin prepared by Bargellini (*loc. cit.*). A number of empirical formulæ agree with the analyses, but without further experiments the selection of a definite formula is not possible. The phenolic *compound* gave with ferric chloride in alcoholic solution a yellow colour, and, like its acetyl derivative, dissolved in concentrated sulphuric acid to a bright yellow solution devoid of fluorescence.—THE UNIVERSITY, MANCHESTER. [*Received, September 13th*, 1927.]

A Double Compound of Chromic and Hydrogen Chlorides. By JAMES RIDDICK PARTINGTON and SIDNEY KEENLYSIDE TWEEDY.

IF a concentrated solution of dark green chromic chloride is mixed with an equal volume of ether and slowly saturated with hydrogen chloride at 0°, the dark green chloride is precipitated. If the saturation is rapid, however, and the cooling bath is dispensed with, the solution becomes warm and besides dark green chromic chloride a heliotrope substance is precipitated. If the mixture is filtered with the aid of a pump, the green chloride often forms a layer of remarkably fine crystals on top of the heliotrope substance. The latter compound may be obtained in a fairly pure state if the stream of gas is stopped when the liquid is homogeneous and brownish-green, and after a while collects at the bottom of the vessel. The mother-liquor is decanted, the residue mixed with a large excess of ether, and after filtration the substance is air-dried. A further crop may be obtained by passing more hydrogen chloride into the mother-liquor, but after three such precipitations the product becomes largely contaminated with dark green chromic chloride. The substance may conveniently be washed with dry ether in a Soxhlet extractor (Found: Cr, 17·8, 17·3; Cl, 44·7, 44·9%. Constant values could not be obtained, showing that the product was never pure).

When freshly precipitated violet chromic chloride is washed with acetone in a Soxhlet extractor, if the acetone is warm when it falls upon the salt the surface of the latter becomes covered with a layer of the heliotrope substance, which in turn becomes covered with a layer of dark green chromic chloride. It would appear, then, that the heliotrope compound is also formed by the action of hydrogen chloride on the violet chloride when warm, since this acid is present in the freshly precipitated chloride.

The analyses agree roughly with the formula $CrCl_3,HCl,6H_2O$, which requires Cr, 17·2; Cl, 46·9%. Contamination with green or violet chromic chloride would cause the chromium content to increase and the chlorine content to decrease. No salts of this general formula have been described, but Larsson (*Z. anorg. Chem.*, 1920, **110**, 153) prepared two salts of composition $CrCl_3,MCl,5H_2O$, where M = Cs and Rb. A compound of this formula with M = H would require Cr, 18·2; Cl, 49·8%. The analyses will not fit in with any other type of double chloride formed by chromic chloride. Until the heliotrope substance can be prepared in a pure state, it can only be said that it is probably a double compound of the formula $CrCl_3,HCl,xH_2O$, where $x = 5$ or 6. The analyses and the method of preparation support the value $x = 6$.

Recoura (*Compt. rend.*, 1886, **102**, 922; *Ann. Chim. Phys.*, 1887, **10**, 49) records that when hydrogen chloride is passed into a chromic chloride solution for some days the latter turns brown and then red, and a soluble compound $CrCl_3,xHCl$ is formed, where x is greater than unity. On addition of ether, however, it is precipitated in unstable, green needles.

The heliotrope substance is insoluble in methyl and ethyl alcohols and dissolves in water to give a pink solution which immediately turns green, although of a different shade from that given by solutions of dark green chromic chloride. If a fragment of the substance is treated with a drop of water and observed under the microscope, it is seen that the process of solution is accompanied by very vigorous turbulence and agitation. It is not proposed at present to investigate the compound any further.—EAST LONDON COLLEGE, LONDON, E. 1. [*Received, October 6th*, 1927.]

The Viscosities of Chromic Anhydride Solutions. By JAMES RIDDICK PARTINGTON and SIDNEY KEENLYSIDE TWEEDY.

CHROMIC anhydride prepared and purified by the authors' method (J., 1926, 1142) had m. p. 193°. Melting points between 170° and 196° have been recorded in the literature. Both capillary-tube and test-tube methods were employed and the thermometer was com-

pared with a standard instrument before use. Groschuff states (*Z. anorg. Chem.*, 1908, **58**, 108) that chromic anhydride supercools to the extent of 26°; our specimens, however, all solidified sharply within a degree or so of the m. p.

The viscosities of solutions of the anhydride were determined with an Ostwald viscometer as modified by Martin (*Bull. Soc. chim. Belg.*, 1925, **34**, 81). The instrument was standardised with conductivity water, and similar water, which had been stored in a Pyrex flask, was used for preparing the solutions. These were obtained by successive dilution. w is the weight of anhydride in 100 g. of water, η is the viscosity of the solution, and η_{H_2O} that of water (in dyne/cm.^{2}).

w.	η/η_{H_2O}.	η.	w.	η/η_{H_2O}.	η.
	Temp. 0°.			Temp. 25°.	
111·4	1·482	—	147·4	2·3360	0·02130
72·86	1·195	—	89·40	1·4880	0·01357
51·38	1·110	—	62·60	1·2480	0·01138
29·59	1·057	—	46·60	1·1600*	0·01058
			42·68	1·1360*	0·01036
	Temp. 18°.		31·67	1·0880	0·009923
98·98	1·5116	0·01616	24·36	1·0560	0·009631
71·01	1·2849	0·01373	12·05	1·024	0·009339
67·22	1·2674	0·01355			
49·59	1·1628	0·01243		Temp. 40°.	
35·92	1·1017	0·01178	111·4	1·328	0·008980
25·63	1·0581	0·01131	72·86	1·164	0·007871
16·71	1·0349	0·01106	51·38	1·1055	0·007475
			29·59	1·053	0·007120
			21·60	1·041	0·007039
			16·55	1·027	0·006945

The readings marked with asterisks appear to be 1—2% too high; they do not lie on the smooth curve passing through the other points. The figures for 40° are probably less trustworthy than those at the lower temperatures, as the thermostat was not automatically controlled at this temperature.

The absolute viscosities, η, were calculated with the aid of Leroux's values for the viscosity of water (*Ann. Physique*, 1925, **4**, 163). If these values are plotted on a very large scale, it is seen that Leroux's results for 2·5° (0·01648) and 7·5° (0·01419 dyne/cm.^{2}) are probably too high by about 0·00015 and 0·0002 dyne/cm.^{2}, respectively. The following equation, which is of the type proposed by Slotte (*Ann. Physik*, 1888, **34**, 28), represents the curve with fair accuracy between 10·9° and 30°:

$$\eta_{H_2O}\ (\text{dyne/cm.}^2) = \frac{0{\cdot}633161}{T - 241{\cdot}307} - 0{\cdot}00207155$$

where $T = t + 273$, t being in degrees Centigrade. The closeness of the observed and calculated values is of the order accepted by Thorpe and Rodger (*Phil. Trans.*, 1894, *A*, **185**, 397):

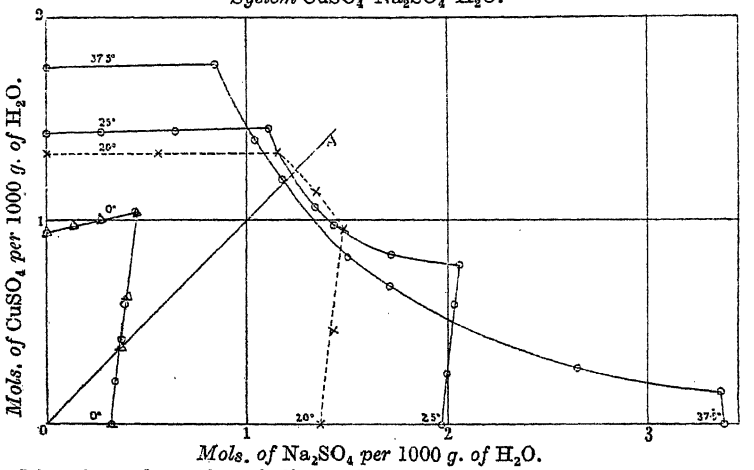
t.	η_{H_2O} (obs.).	(calc.).	t.	η_{H_2O} (obs.).	(calc.).
10·9°	0·01276	0·01279	20°	0·01018	0·010177
14	0·01175	0·01178	23·2	0·00949	0·00946
16	0·01121	0·01120	26·4	0·00883	0·008828
18	0·01069	0·01067	30	0·008198	0·008192

—EAST LONDON COLLEGE, LONDON, E. 1. [*Received, October 6th*, 1927.]

Equilibrium in the System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°. *A Correction.* By ROBERT MARTIN CAVEN and WILLIAM JOHNSTON.

AN error appears in the figures relating to mols. of Na_2SO_4 per 1000 g. of H_2O (this vol., p. 2363), owing to the use of a wrong value for the molecular weight of sodium sulphate. The correct figures are obtained by multiplying those given by the factor 0·838.

System $CuSO_4$–Na_2SO_4–H_2O.



Diacon's results at 0° *are indicated thus* △.
Massink's results at 20° *are indicated thus* ×, *and the isotherm by a broken line.*
0A *is the line of equimolecular proportions to show solubility of double salt.*

Fig. 4 on the same page needs a corresponding adjustment, and the correct figure is shown above.

The error now corrected does not invalidate the conclusions drawn in the paper.—ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, October 15th*, 1927.]

Change of Properties of Substances on Drying. By HERBERT BRERETON BAKER.

MY attention has been directed to a paper by D. Balarew (*J. pr. Chem.*, 1927, **116**, 57). The author sealed up various liquids in

U-tubes, a liquid in one limb and sublimed phosphorus pentoxide in the other, and kept them for 3½ years. He states that subsequent examination of all the liquids, which included hexane and benzene, showed the presence of phosphoric acid, and he suggests that the rise in boiling point which I have found may be due to the presence of this substance or its esters. Apart from the fact that the rise in boiling point which I mentioned (26° in the case of benzene, lately increased to 38°) could not be accounted for by the presence of such an impurity, it was distinctly stated in my paper (J., 1922, **121**, 572) that " In every case the liquid distilled from the dried apparatus was tested for the presence of phosphoric acid, and no trace could be detected." If Balarew's phosphorus pentoxide were not free from the volatile trioxide, his results could be understood.—IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, November 3rd*, 1927.]

The Dimorphism of 2-Chloroaceto-p-toluidide. By MAURICE SCHOFIELD.

2-CHLORO-*p*-NITROTOLUENE (80 g.), m. p. 62·5°, obtained by chlorinating *p*-nitrotoluene (100 g.) at 57—59° in presence of anhydrous ferric chloride (4 g.) and in absence of sunlight and moisture, isolated by pouring the product into water, and crystallised from methylated spirit, was reduced at 60—70° with water (350 c.c.), iron powder (in slight excess; added during 2½ hours), and a little hydrochloric acid. The 2-chloro-*p*-toluidine thus obtained, b. p. 238—240°, m. p. 18°, was acetylated with acetic anhydride and acetic acid. The2-chloroaceto-*p*-toluidide obtained (Found: C, 58·8; H, 5·5; N, 7·5. Calc. for $C_9H_{10}ONCl$: C, 58·8; H, 5·6; N, 7·6%) crystallised from benzene, alcohol, carbon disulphide, ether, and toluene in needles, m. p. 83°. This form, however, crystallised from light petroleum (b. p. 60—80°), in which it was sparingly soluble, in plates, m. p. 104°, and even when it was refluxed with a small quantity of this solvent a bulky, feathery mass, m. p. 104°, was obtained (Found: C, 58·7; H, 5·6; N, 7·7%). The reverse change was effected by crystallising the 104° form from benzene. After the molten 83° form had been kept at 120° for several minutes, solidification occurred at 93° after super-cooling to 89°. No crystallisation took place above 93° if the melt had been kept at 120° for longer periods. Freezing points up to 101° were given by a melt kept under similar conditions and seeded with the 104° form.

Kunckell and Lillig (*J. pr. Chem.*, 1912, **86**, 517) describe 2-chloroaceto-*p*-toluidide as crystallising from benzene in needles, m. p. 104°. —WOLVERHAMPTON AND STAFFORDSHIRE TECHNICAL COLLEGE, WOLVERHAMPTON. [*Received, October 8th*, 1927.]

CCCLXXXVII.—*The Complex Salts of Nickel with Various Aliphatic Diamines.*

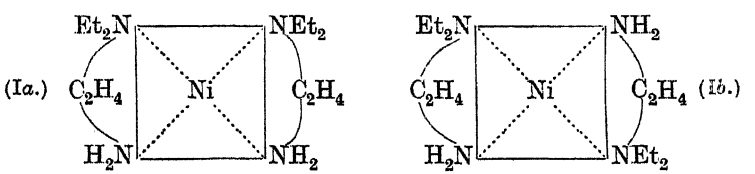
By FREDERICK GEORGE MANN.

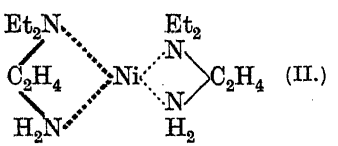
WERNER first suggested (*Z. anorg. Chem.*, 1893, **3**, 298) that when a metal shows a co-ordination number of 6, as in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$, the co-ordinated groups lie at the apices of a regular octahedron described around the metallic atom. The resolution into optically active forms of various complex salts of eight different metals (Co, Cr, Rh, Fe, Pt, Ir, Ru, and Al : also As), all having a co-ordination number of 6, leaves little doubt of the correctness of Werner's views.

Very great uncertainty still exists, however, with regard to the configuration of the complex salts of metals having a co-ordination number of 4, *e.g.*, tetramminonickelous chloride, $[Ni(NH_3)_4]Cl_2$. Biltz and Fetkenheuer (*Z. anorg. Chem.*, 1914, **89**, 121) claim to have prepared two distinct forms of the neutral non-ionic dichlorodiamminocobalt, $[Cl_2Co(NH_3)_2]$, and of the corresponding dibromo- and di-iodo-compounds, a result which would indicate that the four co-ordinated groups lie at the corners of a square with the metallic atom at the centre. This configuration would also explain the existence of two distinct forms of nickel iodate dihydrate, $[(H_2O)_2Ni(IO_3)_2]$ (Meusser, *Ber.*, 1901, **34**, 2438). Tschugaev (*Ber.*, 1906, **39**, 3192), however, failed to detect any similar *cis-trans*-isomerism in a series of salts such as bissuccinimidobismethylaminenickel, $[(C_4H_4O_2N)_2Ni(CH_3{\cdot}NH_2)_2]$. Moreover, the existence of the stable salts, $\beta\beta'\beta''$-triaminotriethylaminenickel thiocyanate, $[NiN(C_2H_4{\cdot}NH_2)_3](SCN)_2$, and $\gamma\gamma'\gamma''$-triaminotripropylaminenickel thiocyanate (Mann and Pope, J., 1926, 482, 489) is more easily explained by assuming that the four co-ordination valencies of the nickel atom are directed to the apices of a regular tetrahedron. Schlesinger (*Ber.*, 1925, **58**, 1877) found that copper, of co-ordination number 4, combines with certain bisimino-carboxylic acids to give compounds existing in two forms, and concludes that the copper complex has therefore the uniplanar configuration, a deduction opposed by Reihlen (*Z. anorg. Chem.*, 1926, **151**, 72), who considers the isomerism to be due to the presence of the two asymmetric nitrogen atoms in these compounds. Moreover, the recent resolution into optically active forms of 4-co-ordination derivatives of copper, zinc, and beryllium by Mills and Gotts (J., 1926, 3121) shows that such metallic complexes have the tetrahedral configuration, thus confirming the conclusions of Lowry and Burgess (J., 1924, **125**, 2081) with regard to the beryllium complex. On the other hand,

the existence of two forms of many derivatives of bivalent platinum and palladium, *e.g.*, dichlorodiamminoplatinum, $[Cl_2Pt(NH_3)_2]$, led Werner (*loc. cit.*, p. 310) to consider that here the complex was uniplanar and the two forms *cis-trans*-isomerides. Reihlen and Nestle (*Annalen*, 1926, **447**, 211) consider these compounds to be merely polymeric forms having the tetrahedral configuration,* a conclusion opposed on experimental grounds by Grunberg (*Z. anorg. Chem.*, 1926, **157**, 299) and Hantzsch (*Ber.*, 1926, **59**, 2761). Finally, the uniplanar configuration has been given to the dimethyltelluronium dihalides by Vernon (J., 1920, **117**, 90) to explain the existence of two isomeric forms.

Attempts were therefore made to obtain more decisive evidence with regard to the configuration of the 4-co-ordination nickel complex by preparing certain complex salts which, if possessing the uniplanar configuration, should show *cis-trans*-isomerism, and, if possessing the tetrahedral configuration, should be resolvable into optically active forms. Nickel was first combined with β-aminotriethylamine to give *bis-β-aminotriethylaminenickelous thiocyanate*, $[Ni\{(C_2H_5)_2N\cdot C_2H_4\cdot NH_2\}_2](SCN)_2$. This compound, if possessing the uniplanar configuration, should exist in the *cis* (I*a*)





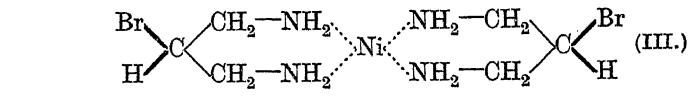
and the *trans* (I*b*) form, whilst if possessing the tetrahedral configuration (II),† it should be resolvable into optically active forms owing to its dissymmetric nature. No evidence of *cis-trans*-isomerism could be detected in this compound, whilst the presence of the tertiary nitrogen atoms rendered the complex so unstable that attempts at resolution could not be completed.

In order to avoid the presence of tertiary nitrogen atoms, a new type of complex salt was prepared by co-ordinating nickel with β-bromo-αγ-diaminopropane to give *bis-β-bromo-αγ-diaminopropane-*

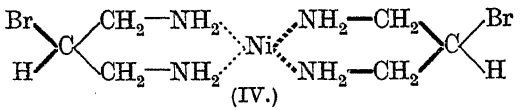
* Reihlen goes further and states (*Annalen*, 1926, **448**, 316) that all 4-co-ordination elements have the tetrahedral configuration.

† The thick bonds are in the plane of the paper, the thin ones at right angles to it.

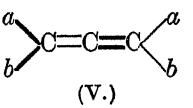
nickelous thiocyanate, $[\{(NH_2\cdot CH_2)_2CHBr\}_2Ni](SCN)_2$. If this complex has the uniplanar configuration, the two co-ordinated ring systems lie in one plane, which is at right angles to that in which the terminal bromine and hydrogen atoms lie : the complex should therefore show *cis-trans*-isomerism according as the two bromine atoms are both on one side of the co-ordinated plane (III) or are on opposite sides, respectively. If, however, the complex has the



(III.)



(IV.)



(V.)

tetrahedral configuration, the two ring systems are at right angles to each other (IV) : the complex thus possesses molecular dissymmetry, being structurally of the same type as the allene compounds (V), and should be resolvable into optically active forms. Here again, however, the highly crystalline dithiocyanate showed no signs of *cis-trans*-isomerism, whilst attempts at resolution failed because of the labile character of the bromine atoms; *e.g.*, the bis-β-bromo-αγ-diaminopropanenickelous thiocyanate in hot aqueous solution changed rapidly into the highly crystalline *bis-β-thiocyano-αγ-diaminopropanenickelous thiocyanate*,

$$[\{(NH_2\cdot CH_2)_2CH(SCN)\}_2Ni](SCN)_2.$$

Although this compound is of the required type for the purposes of this investigation, its low solubility in water made it unsuitable for use. Attempts were made to join a more stable group to the central carbon atom, and in particular to prepare αγ-diamino-*iso*propyl methyl ether, $(NH_2\cdot CH_2)_2CH\cdot O\cdot CH_3$. αγ-Dichlorohydrin reacts readily with potassium phthalimide to give αγ-diphthalimido-*iso*propyl alcohol, $(C_6H_4<^{CO}_{CO}>N\cdot CH_2)_2CH\cdot OH$: the hydroxyl group is, however, so well protected (probably sterically) that it is extremely inert and could not be methylated. Dichlorohydrin was itself methylated to give dichloro*iso*propyl methyl ether (Hess and Fink, *Ber.*, 1915, **48**, 2003), but the chlorine atoms were now extremely inert and would not react with potassium phthalimide even when heated in a sealed tube at 180° for 4 hours.

Nickel was next combined with the easily obtained αγ-diamino-*iso*propyl alcohol to give *bis-αγ-diamino-β-hydroxypropanenickelous thiocyanate*, $[\{(NH_2\cdot CH_2)_2CH\cdot OH\}_2Ni](SCN)_2$. Since, however, bivalent nickel may show a co-ordination number of 4 or of 6, it is difficult to decide whether in this compound the nickel has a

co-ordination number of 4 and is combined solely with the four amino-groups, or of 6 and is combined with the four amino-groups and with the two hydroxyl groups. It was found, however, that the diamine co-ordinates with cobalt to give *dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic monochloride*,

$$[\{(NH_2\cdot CH_2)_2CH\cdot OH\}_2Co(OH)_2]Cl,$$

a compound in which the alcohol molecules must be co-ordinated by the amino-groups alone, and it was considered probable that the same held true of the above nickel compound, which should therefore be of the desired type. Again, however, no trace of *cis-trans*-isomerism was detected, and all attempts at resolution failed.

β-*Methyltrimethylenediamine* was now synthesised by converting β-methyltrimethylene dibromide into the corresponding *diphthalimido*-compound and hydrolysing it. The diamine was combined with nickel to give *bis-β-methyltrimethylenediaminenickelous thiocyanate*, $[\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2Ni](SCN)_2$. This compound, although highly crystalline, showed no evidence of *cis-trans*-isomerism, and all attempts at resolution again failed.

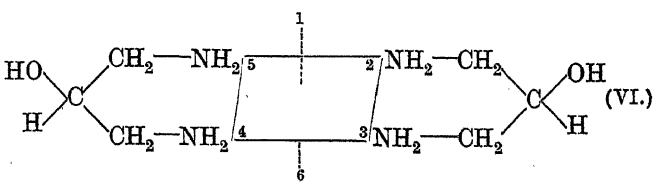
These repeated failures to resolve the nickel compounds may have been due either to the complex possessing the uniplanar configuration, or to the complex, if dissymmetric, undergoing such rapid racemisation that no evidence of resolution could be detected. The latter is presumably the reason for repeated failures in the past to resolve 6-co-ordination nickel derivatives, *e.g.*, trisethylenediaminenickel salts, and also tristriaminotriethylaminebisnickelous salts (Mann and Pope, *loc. cit.*, p. 486).

An interesting point arises here. It is well known that the complex compounds of nickel in which the metal has a co-ordination number of 4 are much more stable than those in which the co-ordination number is 6: yet nickel will combine with three molecules of the simplest aliphatic diamines, *e.g.*, ethylenediamine and propylenediamine, to give compounds such as trisethylenediaminenickel chloride, $[Ni\,en_3]Cl_2$, which are sufficiently stable to be isolated and sometimes even recrystallised, in spite of the fact that the metal here has a co-ordination number of 6. Yet in the present investigation it was found that even if a nickel salt (nickel chloride in aqueous solution: nickel succinimide in alcoholic solution) was treated with a very large excess of the various diamines employed, *viz.*, β-aminotriethylamine, αγ-diamino*iso*propyl alcohol, and β-methyltrimethylenediamine, only two molecules of the diamine co-ordinated with the metal and no trace of a compound in which the metal had a co-ordination number of 6 could be isolated. Similarly *roseo*cobaltic chloride on treatment with a large excess of diamino*iso*propyl alcohol gave always dihydroxybisdiaminohydroxy-

propanecobaltic monochloride, and again no compound in which three molecules of the diamine co-ordinated with the cobalt atom could be prepared. Many similar instances have previously been recorded. Thus nickel combines with only two molecules of dimethylglyoxime, to give $[Ni(ON{:}CMe{\cdot}CMe{:}N{\cdot}OH)_2]$, and never with three molecules, whilst cobalt will give diamminobisdimethylglyoximecobaltic monochloride, $[(ON{:}CMe{\cdot}CMe{:}N{\cdot}OH)_2Co(NH_3)_2]Cl$, but will not combine with three molecules of the dioxime. Dicyanodiamidine gives diaquobisdicyanodiamidinenickel,

$$[\{NH_2{\cdot}(NH{:})C{\cdot}N{\cdot}CO{\cdot}NH_2\}_2Ni(H_2O)_2],$$

but the two molecules of water cannot be replaced by a third molecule of the diamidine. This inability of nickel * to combine with more than two molecules of any but the simplest double-bridging groups cannot be ascribed to the general instability of 6-co-ordination nickel compounds, since tristriaminotriethylaminebisnickelous tetraiodide is a very stable compound, in spite of the presence of two weakly co-ordinating aliphatic tertiary nitrogen atoms: it is more probably due to the difficult access of the third molecule of the diamine. Thus if, when nickel is treated with an excess of, *e.g.*, diamino*iso*propyl alcohol, two molecules of the diamine co-ordinate first to give a 4-co-ordination complex having the uniplanar configuration (VI), co-ordination of a third molecule of the diamine



(VI.)

would involve bridging the potential 1 : 6-positions, which is structurally probably impossible. Similarly, with tervalent cobalt it is probable that the first two molecules of the diamine again occupy the 2 : 3- and 4 : 5-positions respectively; whence the distant 1- and 6-positions have to be occupied by simple unbridged groups as in dihydroxybisdiaminohydroxypropanecobaltic chloride and diamminobisdimethylglyoximecobaltic chloride.

Although the extreme difficulty of co-ordinating a third double-bridging group to the nickel atom can thus be explained on the assumption that the 4-co-ordination nickel complex has the uniplanar configuration, it is, on the other hand, significant that in the present investigation the five different complex salts showed no

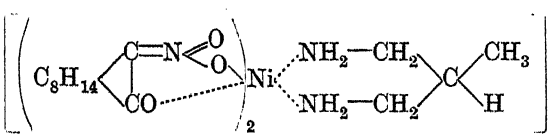
* Tervalent cobalt does not always share this inability: it will combine, *e.g.*, with 3 molecules of α-nitroso-β-naphthol (Morgan and Smith, J., 1921, **119**, 704).

evidence of *cis-trans*-isomerism, although all were highly crystalline compounds in which such isomerism should have been easily detected. The evidence for the configuration of the nickel complex thus remains conflicting.

A novel and apparently quite general reaction of 4-co-ordination nickel salts arose in the present investigation. Werner, in order to resolve certain complex salts of chromium (*Ber.*, 1912, **45**, 865), had recourse to crystallisation of the camphornitronates of the complex, prepared by simple double decomposition with the normal salts. Similar attempts were made with these nickel complex salts, since crystallisation of the camphorsulphonates had failed to effect resolution. When, however, bis-β-methyltrimethylenediaminenickelous nitrate is treated in cold aqueous solution with an excess of ammonium nitrocamphor, ammonia is at once liberated, the solution changes in colour from deep blue to green, and a rapid precipitation of the green, neutral, non-ionic *biscamphornitronate-β-methyltrimethylenediaminenickel* occurs, in accordance with the equation

$$[Ni\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2](NO_3)_2 + 2C_{10}H_{14}O\cdot NO_2NH_4 = [(C_{10}H_{14}O\cdot NO_2)_2Ni\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}] + CH_3\cdot CH(CH_2\cdot NH_2,HNO_3)_2 + 2NH_3.$$

A precisely similar reaction occurs with the corresponding compounds of β-aminotriethylamine and diamino*iso*propyl alcohol, thus providing further evidence that the latter diamine occupies only two co-ordination positions, *i.e.*, is co-ordinated by the amino-groups alone and not by the hydroxyl group. The three compounds so obtained are soluble in the usual organic liquids, but insoluble in water, a property common to many neutral, non-ionic co-ordination compounds. It is probable that in these compounds the ketonic group in the camphor molecule is also linked by a subsidiary valency to the nickel atom, which has therefore a co-ordination number of 6 (VII). In this case the complex as a whole becomes



(VII.)

dissymmetric (in addition to the dissymmetric character of the constituent camphor residues) and the recrystallised compounds in solution might be expected to show mutarotation owing to slow racemisation of the complex itself. No such mutarotation was shown in chloroform solution, however, by the three compounds of this type available.

It is obvious that the new diamine, β-methyltrimethylenediamine, should prove extremely useful in the solution of various problems connected with the stereochemistry of complex salts. Its use will unfortunately be limited, because the preparation of β-methyltrimethylene dibromide is extremely slow and tedious and the yield of the diphthalimido-compound is very small owing to side reactions. The diamine, however, co-ordinates with bivalent platinum to give *bis*-β-*methyltrimethylenediamineplatinous chloride*, $[Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2]Cl_2$. This compound is now being further investigated, since the occurrence of *cis-trans*-isomerism or of optical activity would solve the vexed question of the configuration of the complex platinous salts.

Experimental.

All rotations given in this paper have been measured at 15° in a 4-dcm. polarimeter tube.

The Complex Salts of β-*Aminotriethylamine.*

β-*Aminotriethylamine*, $N(C_2H_5)_2\cdot CH_2\cdot CH_2\cdot NH_2$.—In view of the low solubility of phthal-β-bromoethylimide in diethylamine, Ristenpart's preparation of this base can with advantage be modified as follows : Phthal-β-bromoethylimide (23 g.), diethylamine (18·3 c.c.), and anhydrous xylene (50 c.c.) were confined in a round-bottomed bottle and heated at 100° for 10 hours, diethylamine hydrobromide slowly crystallising from the clear solution. The cold mixture was acidified with hydrochloric acid (1 : 1 by vol.), the xylene removed by steam distillation, and the residue hydrolysed by boiling under reflux, with the addition of fresh acid, for 3 hours. The product was then made alkaline and steam-distilled. The mixture of bases which separated when the distillate was saturated with potassium hydroxide was dried over fresh potash and then fractionally distilled. β-Aminotriethylamine was obtained as a colourless liquid, b. p. 144—146°.

Bis-β-*aminotriethylaminenickelous Thiocyanate.*—β-Aminotriethylamine (15·8 c.c.; 3 mols.) was added to a solution of nickel succinimide (15·0 g.) in hot absolute alcohol (500 c.c.), and the whole boiled under reflux for 4 hours. The cooled filtrate from the concentrated solution, when treated with an equal volume of a saturated alcoholic solution (90%) of potassium thiocyanate, yielded almost immediately the above *thiocyanate*, which, after 3 hours, was washed with water, alcohol, and ether (yield 10·4 g., *i.e.*, 68% calculated on the nickel taken). The yield was considerably decreased if the alcohol used in the preparation was not absolute, or if the above large excess of the amine was not employed. In spite of this excess,

no compound in which the nickel had combined with more than two molecules of the amine could be isolated. The thiocyanate crystallised from absolute alcohol in lilac-blue needles, m. p. 213—214° (decomp.) after shrinking at 204° (Found: C, 41·5; H, 8·0; N, 20·7; Ni, 14·4. $C_{14}H_{32}N_6S_2Ni$ requires C, 41·3; H, 7·9; N, 20·65; Ni, 14·4%).

The *chloroplatinate*, $[\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2Ni]PtCl_6$, was precipitated on addition of a solution of the thiocyanate (0·5 g.) in acetone (35 c.c.) to a solution of sodium chloroplatinate (0·9 g.) in water (5 c.c.) and acetone (30 c.c.), and was obtained, after being washed with water, acetone and ether, as an apricot-coloured powder, insoluble in boiling water and alcohol. It darkens at 165—168° and shrinks to a plastic rod at 179—181° (Found: C, 20·4; H, 4·6. $C_{12}H_{32}N_4Cl_6NiPt$ requires C, 20·6; H, 4·6%).

Attempted Preparation of the d-*Camphor-β-sulphonate of the Complex.*—Hot solutions of bisaminotriethylaminenickelous thiocyanate (5 g.) in alcohol (300 c.c.) and of silver *d*-camphorsulphonate (8·3 g.) in alcohol (100 c.c.) were mixed, boiled for 5 minutes, and filtered. The fine, very pale blue, crystalline precipitate deposited on cooling was difficult to filter off and recrystallise. Eventually, 1 g. portions were dissolved in a little boiling absolute alcohol, and the solutions filtered quickly. The filtrates deposited very pale blue (almost white) crystals, m. p. 175—176°. This very pale blue colour is characteristic of many neutral non-ionic nickel complex salts, such as nickel succinimide, $[(H_2O)_2Ni(NC_4H_4O_2)_2]$: the camphorsulphonate, moreover, in alcoholic solution gave no precipitate with sodium chloroplatinate, although the chloroplatinate of the complex $[\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2Ni]''$ is insoluble in alcohol. It is probable, therefore, that the camphorsulphonate radicals had entered the complex, and the nickel had thus increased its co-ordination number to 6, giving the neutral non-ionic *bis*-d-*camphorsulphonatebisaminotriethylaminenickel*,

$$[(C_{10}H_{15}O\cdot SO_3)_2Ni\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2]$$

(Found: N, 7·4; S, 8·4; Ni, 7·45. $C_{32}H_{62}O_8N_4S_2Ni$ requires N, 7·4; S, 8·5; Ni, 7·8%).

The d-*α-bromocamphor-π-sulphonate* was obtained from the thiocyanate (5 g. in hot alcohol, 300 c.c.) and silver *d*-α-bromocamphor-π-sulphonate (10·7 g. in alcohol, 150 c.c.), the conditions and difficulties of the preparation being similar to those described above. Also, for reasons similar to those mentioned above, the very pale blue product, m. p. 165—168° (decomp.), probably has the constitution $[(C_{10}H_{14}BrO\cdot SO_3)_2Ni\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2]$ (Found: N, 5·9; Ni, 6·7, 6·65. $C_{32}H_{60}O_8N_4S_2Br_2Ni$ requires N, 6·15; Ni, 6·4%).

The alcoholic solution from which this compound originally separated was concentrated and cooled, and the precipitate of the nickel complex compound filtered off. The filtrate was evaporated to dryness, and the residue twice recrystallised from benzene, from which the d-*α-bromocamphorsulphonate* of *β-aminotriethylammonium hydroxide*, $(C_{10}H_{14}OBr\cdot SO_3H,NH_2\cdot C_2H_4)\cdot NH(C_2H_5)_2\cdot OH$ separated in white crystals, m. p. 80—82° (Found: C, 43·5; H, 7·4; N, 6·5; Br, 17·9. $C_{16}H_{33}O_5N_2BrS$ requires C, 43·15; H, 7·5; N, 6·3; Br, 17·95%). The identity of this compound was confirmed by mixed melting-point determinations with the product obtained by treating bromocamphorsulphonic acid in alcoholic solution with an excess of the base, evaporating the solution to dryness, and recrystallising the residue from benzene. The presence of this compound in the original preparation shows that further decomposition of the complex occurs in hot alcoholic solution, the diamine being split off from the metal and becoming partially neutralised by the sulphonic acid.

Bis-d-*camphornitronateaminotriethylaminenickel*,

$$[(C_{10}H_{14}O\cdot NO_2)_2NiN(C_2H_5)_2\cdot C_2H_4\cdot NH_2].$$

—Finely-powdered silver *d*-camphornitronate (4·5 g.) was added to a solution of bis-β-aminotriethylaminenickelous thiocyanate (3·0 g.) in boiling alcohol (300 c.c.). After being boiled for 10 minutes and filtered, the deep olive-green solution was evaporated under reduced pressure to small bulk, again filtered, and then diluted with a little hot water. The precipitate was recrystallised from hot aqueous alcohol (95%), and the product thus obtained in deep olive-green crystals, m. p. 258—260° (decomp.) after softening at 248° (Found: C, 54·9; H, 7·6; N, 9·8. $C_{26}H_{44}O_6N_4Ni$ requires C, 55·0; H, 7·8; N, 9·9%). A 0·212% solution in chloroform had $\alpha_{5461} + 2·33°$, whence $[\alpha]_{5461} + 275°$, and $[M]_{5461} + 1560°$: this rotation remained unchanged for 20 hours.

The Complex Salts of β-Bromo-αγ-diaminopropane.

β-Bromo-αγ-diaminopropane, $(NH_2\cdot CH_2)_2CHBr$.—Gabriel's preparation of the dihydrobromide of this base (*Ber.*, 1889, **22**, 225) was modified as follows: A mixture of diphthalimido*iso*propyl alcohol (7·0 g.) and a saturated solution of hydrogen bromide in acetic acid (23 c.c.) was heated in a sealed tube at 100° for 30 hours with occasional shaking. After cooling, the precipitate was filtered off, washed with alcohol, and recrystallised from acetic acid, from which *αγ-diphthalimido*iso*propyl bromide* separated in colourless crystals, m. p. 196—198° (Found: N, 6·6; Br, 19·2. $C_{19}H_{13}O_4N_2Br$ requires N, 6·8; Br, 19·3%). This compound was boiled under reflux with hydrobromic acid of constant b. p., and the clear solution

was chilled, filtered from phthalic acid, and evaporated until, on cooling, the dihydrobromide of β-bromo-αγ-diaminopropane crystallised. The latter, when washed with alcohol and dried, was pure.

Bis-β-bromo-αγ-diaminopropanenickelous Thiocyanate.—A solution of β-bromo-αγ-diaminopropane dihydrobromide (13·0 g.) in 15% aqueous sodium hydroxide (19·0 c.c.) was added to one of nickel succinimide (6·0 g.) in boiling alcohol (240 c.c.), the green colour of the nickel solution changing at once to blue. The solution was boiled for 15 minutes, filtered, reduced to small bulk, and treated with a saturated solution of potassium thiocyanate in 95% alcohol. The precipitate was filtered off after 2 hours and washed with water, alcohol and ether. The *thiocyanate* was thus obtained as a fine pink powder, m. p. 200—203° (decomp.) after shrinking and darkening at 160°. It is insoluble in all the usual organic liquids, and is decomposed by hot water (Found: C, 20·0; H, 3·8; Br, 33·2; Ni, 12·2. $C_8H_{18}N_6Br_2S_2Ni$ requires C, 20·0; H, 3·8; Br, 33·25; Ni, 12·2%). If this compound is kept in contact with the original solution for more than 2 hours, it becomes contaminated with deep blue crystals of *bis-β-thiocyano-αγ-diaminopropanenickelous thiocyanate*. The latter compound was obtained pure by boiling bis-β-bromo-αγ-diaminopropanenickelous thiocyanate with water, a deep blue solution being obtained. The concentrated solution on quick cooling gave a fine blue, crystalline powder, whilst the dilute solution on slow cooling gave deep blue, heavy prisms; both deposits, after being washed with water, alcohol and ether, had m. p. 247—248° (decomp.) (Found: C, 27·5, 27·6; H, 4·4, 4·3; S, 29·4; Ni, 13·4. $C_{10}H_{18}N_8S_4Ni$ requires C, 27·5; H, 4·15; S, 29·3; Ni, 13·4%).

αγ-Dichloro*iso*propyl methyl ether, $(CH_2Cl)_2CH{\cdot}O{\cdot}CH_3$, was obtained as a colourless liquid, b. p. 66·5—67°/24 mm., having a characteristic peppermint-like odour (Found: C, 33·5; H, 5·7. Calc. for $C_4H_8OCl_2$: C, 33·6; H, 5·6%). When it was heated with an excess of potassium phthalimide in a sealed tube at 180° for 4 hours, much remained unchanged and no diphthalimido-derivative could be isolated.

*The Complex Salts of αγ-Diamino*iso*propyl Alcohol.*

*αγ-Diamino*iso*propyl Alcohol Dihydrochloride,* $(CH_2{\cdot}NH_2,HCl)_2CH{\cdot}OH$.—Diphthalimido*iso*propyl alcohol, prepared by Gabriel's method (*Ber.*, 1889, **22**, 224), was boiled under reflux with concentrated hydrochloric acid; the clear solution obtained, when chilled, filtered, and evaporated, gave the pure crystalline dihydrochloride.

Dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic Monochloride.—A solution of diamino*iso*propyl alcohol dihydrochloride (12·2 g.; 2 mols.) in 10% aqueous sodium hydroxide (59 c.c.) was added to a mixture of *roseo*-cobaltic chloride (10 g.) and water (150 c.c.), and the whole heated under reflux on a water-bath for 3 hours, ammonia being freely evolved. The solution was then boiled for 30 minutes, filtered, and evaporated until crystals appeared. After cooling, the latter were collected and recrystallised from hot water, the *cobaltic monochloride* separating in dark red needles (Found: C, 23·6; H, 7·2; N, 17·9; Cl, 11·6. $C_6H_{22}O_4N_4ClCo$ requires C, 23·3; H, 7·2; N, 18·1; Cl, 11·5%). If the original solution was treated with potassium thiocyanate before the chloride started to crystallise, the corresponding *monothiocyanate* separated; after recrystallisation from water, it was obtained in fine, dark red crystals, decomp. 240—250° after shrinking at about 230° (Found: C, 25·2; H, 6·7; N, 21·0. $C_7H_{22}O_4N_5SCo$ requires C, 25·3; H, 6·7; N, 21·1%). A solution of the pure chloride, when treated with potassium iodide, gave the *monoiodide*, which also recrystallised from water in deep red leaflets (Found: C, 18·1; H, 5·5; I, 31·5. $C_6H_{22}O_4N_4ICo$ requires C, 18·0; H, 5·5; I, 31·7%).

Bis-αγ-diamino-β-hydroxypropanenickelous Thiocyanate.—A solution of diamino*iso*propyl alcohol dihydrochloride (17 g.) in water (50 c.c.) was treated with 10% aqueous sodium hydroxide (80·5 c.c.), and the whole added to a solution of hydrated nickel chloride (12 g.) in water (100 c.c.). The solution so obtained was heated under reflux on a water-bath for 4 hours, filtered, and concentrated. The addition of potassium thiocyanate solution gave the *thiocyanate* as a violet precipitate, which separated from hot water as a pale violet, crystalline powder, m. p. (to a clear blue liquid) 161—163° after shrinking at 105° (Found: C, 27·2; H, 5·6; N, 23·4; Ni, 16·7. $C_8H_{20}O_2N_6S_2Ni$ requires C, 27·1; H, 5·7; N, 23·7; Ni, 16·5%).

The original solution, when diluted with potassium iodide solution, slowly deposited the corresponding *di-iodide*, which separated from water, in which it was very soluble, in deep bluish-violet crystals, m. p. 239—242° (decomp.) (Found: C, 14·7; H, 4·1; I, 51·4. $C_6H_{20}O_2N_4I_2Ni$ requires C, 14·6; H, 4·1; I, 51·5%).

Bis-αγ-diamino-β-hydroxypropanenickelous d-*Camphor-β-sulphonate*, $[\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}_2Ni](C_{10}H_{15}O{\cdot}SO_3)_2$.—Hot aqueous solutions of the thiocyanate (10 g.) and of silver *d*-camphorsulphonate (19·2 g.) were mixed, boiled for 5 minutes, filtered, and evaporated to dryness. The powdered residue was recrystallised from alcohol (charcoal), and the d-*camphor-β-sulphonate* obtained in pale lilac-blue crystals (Found: N, 8·2, 8·1; Ni, 8·6. $C_{26}H_{50}O_{10}N_4S_2Ni$ requires N, 8·0; Ni, 8·4%).

This camphorsulphonate was recrystallised seven times from alcohol, and its rotation for the mercury violet line (the only light which would penetrate the deep violet solutions) was then compared with those of the actual specimens of highly purified zinc and magnesium dicamphorsulphonates which Graham (J., 1912, **101**, 746) had prepared for rotatory determinations. The following readings were all made at 15° in a 4-dcm. tube. $\lambda = 4062$; c = concentration of the solution in g./100 c.c.; A denotes $C_{10}H_{15}O{\cdot}SO_3$.

Substance.	c.	α.	$[\alpha]$.	$[M]$.
$[\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}_2Ni]A_2$ ...	1·7466	+3·60°	+51·5°	+361°
$MgA_2,6H_2O$	1·8824	+4·60	+61·1	+363
$ZnA_2,6H_2O$	1·8699	+4·25	+56·8	+361

These results show that the activity of the complex nickel salt is due solely to the camphorsulphonate radicals, and not to the complex itself. This was confirmed by reconverting the camphorsulphonate into the thiocyanate: the latter was inactive.

Bis-d-*camphornitronate*-$\alpha\gamma$-*diamino*-β-*hydroxypropanenickel*, $[(C_{10}H_{14}O{\cdot}NO_2)_2Ni\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}]$.—Hot aqueous solutions of the above thiocyanate and of silver nitrate (2 mols.) were mixed, boiled for 5 minutes, filtered, concentrated and chilled, a solution of the very soluble bis-$\alpha\gamma$-diamino-β-hydroxypropanenickelous nitrate being thus obtained. The addition of a concentrated cold aqueous solution of ammonium nitrocamphor (2·5 mols.) caused the violet colour to change immediately to green, and the solution, after 12 hours, deposited a fine, green precipitate. This, when dry, was soluble in nearly all the usual organic solvents: it was finally recrystallised from anhydrous benzene, from which *bis*-d-*camphornitronate*-$\alpha\gamma$-*diamino*-β-*hydroxypropanenickel* separated as a fine, olive-green powder with a molecule of benzene of crystallisation (Found: C, 56·5; H, 7·2; Ni, 9·3; C_6H_6, 12·3. $C_{29}H_{44}O_7N_4Ni$ requires C, 56·25; H, 7·2; Ni, 9·5; C_6H_6, 12·6%), which was lost in a vacuum at 80°, leaving the pure product as an olive-green powder; this shrank and blackened up to 210° (Found: C, 51·2; H, 7·0; Ni, 10·8. $C_{23}H_{38}O_7N_4Ni$ requires C, 51·0; H, 7·05; Ni, 10·85%). A 0·272% solution of the benzene-free material in chloroform had $\alpha_{5461} + 2{\cdot}89°$, whence $[\alpha]_{5461} + 266°$ and $[M]_{5461} + 1440°$. No change in rotation occurred during 20 hours.

The Complex Salts of β-*Methyltrimethylenediamine.*

$\alpha\gamma$-*Diphthalimido*-β-*methylpropane*, $CH_3{\cdot}CH(CH_2{\cdot}N{:}C_2O_2{:}C_6H_4)_2$.—A uniform mixture of potassium phthalimide (32 g.) and β-methyltrimethylene dibromide (Faworski, *Annalen*, 1907, **354**, 384) (10 c.c.) was heated at 175—180° for 6 hours. The cold product was pulverised and extracted twice with boiling carbon tetrachloride

(200 + 80 c.c.), giving 16 + 1·5 g. of the crude diphthalimido-compound and leaving a residue of potassium bromide and a small quantity of phthalimide. The phthalimido-compound was twice crystallised from boiling alcohol (400 c.c. each time), and *αγ-diphthalimido-β-methylpropane* obtained in fine, white, crystalline scales, m. p. 169—171° (Found: C, 68·8; H, 4·8; N, 8·1. $C_{20}H_{16}O_4N_2$ requires C, 68·9; H, 4·6; N, 8·05%).

β-Methyltrimethylenediamine Dihydrochloride,

$$CH_3{\cdot}CH(CH_2{\cdot}NH_2,HCl)_2.$$

—αγ-Diphthalimido-β-methylpropane (12 g.) and concentrated hydrochloric acid (50 c.c.), heated in a sealed tube at 160° for 18 hours, the tube being inverted from time to time to mix the contents, gave a clear pale brown solution; this, when cold, was filtered from phthalic acid and concentrated. The *dihydrochloride* was now obtained in three successive crops by (*a*) crystallisation from the concentrated aqueous solution, (*b*) diluting the filtrate from the first crop with alcohol, and (*c*) further dilution with ether [Found: (*a*) Cl, 43·9, (*b*) C, 29·8; H, 8·7; Cl, 44·0, (*c*) Cl, 43·9. $C_4H_{14}N_2Cl_2$ requires C, 29·8; H, 8·8; Cl, 44·0%]. It separated in deliquescent, fine, white crystals, m. p. 195—197°, very soluble in water, but insoluble in alcohol and ether.

The *dihydrobromide* was similarly obtained by means of concentrated hydrobromic acid, and separated, when the final concentrated solution was diluted with alcohol, in colourless needles, m. p. 227—229° (decomp.) (Found: Br, 64·0. $C_4H_{14}N_2Br_2$ requires Br, 64·0%).

The *dibenzoyl* derivative, $CH_3{\cdot}CH(CH_2{\cdot}NHBz)_2$, prepared in the usual way, after crystallising twice from benzene and once from acetone, was obtained in fine, white crystals, which melted with effervescence at 92—93°, rapidly resolidified, and remelted at 136—138° (Found: C, 73·2; H, 6·85. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8%).

Bis-β-methyltrimethylenediaminenickelous Thiocyanate.—A mixture of a solution of β-methyltrimethylenediamine dihydrochloride (9·0 g.; 2·2 mols.) in 10% aqueous sodium hydroxide (20 c.c.) with a solution of nickel succinimide (10 g.) in boiling alcohol (300 c.c.) rapidly became blue. It was boiled under reflux for 1 hour, filtered from a small quantity of an apple-green precipitate, and concentrated. The cold solution, on treatment with a concentrated aqueous solution of potassium thiocyanate, rapidly gave a bluish-red precipitate of the thiocyanate of the nickel complex. The latter can be recrystallised quickly from hot water, but prolonged boiling causes the precipitation of a green sludge. After two recrystallisations, the *thiocyanate* was obtained in deep blue needles,

m. p. 226—228° (decomp.) (Found: C, 33·9; H, 6·9; N, 24·0. $C_{10}H_{24}N_6S_2Ni$ requires C, 34·2; H, 6·9; N, 23·9%).

Bis-β-methyltrimethylenediaminenickelous d-*Camphor-β-sulphonate*, $[Ni\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2](C_{10}H_{15}O\cdot SO_3)_2$.—Solutions of the above thiocyanate (6 g.) in hot water (120 c.c.) and of silver *d*-camphorsulphonate (11·8 g.) in water (100 c.c.) were slowly mixed and then boiled for 5 minutes. Filtration gave a clear blue solution which, when concentrated and chilled, furnished the d-*camphorsulphonate* in fine, lilac-blue scales. These were recrystallised twice from alcohol, and then had m. p. 287—288° (decomp.) (Found: C, 48·5; H, 7·7; N, 8·05; Ni, 8·4. $C_{28}H_{54}O_8N_4S_2Ni$ requires C, 48·2; H, 7·8; N, 8·0; Ni, 8·4%). This material was recrystallised seven times from alcohol, and so obtained as pale blue, minute crystals (Found: C, 48·3; H, 7·7%): a 1·098% aqueous solution had $\alpha_{4062} + 2·11°$, whence $[\alpha]_{4062} + 48·0°$ and $[M]_{4062} + 335°$. This sulphonate was reconverted in cold aqueous solution into the thiocyanate, which was inactive. A further preparation of the camphorsulphonate was recrystallised six times from water, and so obtained as the *monohydrate* (Found: C, 46·8; H, 8·2.

$$C_{28}H_{54}O_8N_4S_2Ni,H_2O$$

requires C, 47·0; H, 7·9%): this, in 1·059% aqueous solution, had $\alpha_{4062} + 2·17°$, whence $[\alpha]_{4062} + 51·2°$ and $[M]_{4062} + 366°$, but once again furnished an inactive thiocyanate.

Bis-d-*camphornitronate-β-methyltrimethylenediaminenickel*, $[(C_{10}H_{14}O\cdot NO_2)_2Ni\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}]$.—A solution of the *d*-camphorsulphonate (5 g.) in water (50 c.c.) was treated with an excess of ammonium nitrocamphor (3·5 g.), also dissolved in water (25 c.c.). A green precipitate rapidly appeared, and the solution smelt strongly of ammonia. The precipitate was washed with water and recrystallised from alcohol, from which the *nitronate* separated in fine, olive-green crystals, m. p. 293—295° (decomp.) (Found: C, 53·4; H, 7·4; Ni, 10·8. $C_{24}H_{40}O_6N_4Ni$ requires C, 53·4; H, 7·5; Ni, 10·9%). A 0·273% solution in chloroform had $\alpha_{5461} + 3·52°$, whence $[\alpha]_{5461} + 322°$ and $[M]_{5461} + 1736°$: the activity remained unchanged for 24 hours. This compound is only slightly soluble in water, but is soluble in nearly all the usual organic solvents.

The Complex Salts of β-Methyltrimethylenediamine with Bivalent Platinum.—A solution of ammonium chloroplatinite (4 g.) in water (20 c.c.) was added to one of methyltrimethylenediamine dihydrochloride (5·4 g.; 3 mols.) in 10% aqueous sodium hydroxide (12·8 c.c.). A pale yellow precipitate slowly separated, and after 2 hours the mixture was heated under reflux on a water-bath for a further 8 hours, and then chilled. The precipitate was filtered off and recrystallised from hot water, from which *dichloro-β-methyl*-

methylenediamineplatinum, $[Cl_2Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}]$, separated in very pale yellow crystals, m. p. 273—276° (decomp.) (Found: C, 13·5; H, 3·45; Pt, 55·0. $C_4H_{12}N_2Cl_2Pt$ requires C, 13·5; H, 3·4; Pt, 55·1%). The original filtrate was now evaporated to about half its original volume, and on quick cooling, *bis*-β-*methyltrimethylenediamineplatinous chloride*, $[Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2]Cl_2$, separated as a fine, white, crystalline powder, m. p. 266—267° (decomp.) after darkening at about 240° (Found: C, 21·4; H, 5·45; Pt, 44·2. $C_8H_{24}N_4Cl_2Pt$ requires C, 21·7; H, 5·5; Pt, 44·1%). The filtrate, on standing several days, deposited a mixture of colourless crystals of sodium chloride and very pale yellow crystals of the platinous dichloride compound. The latter could be very easily separated by hand, and no indication of *cis-trans*-isomeric forms could be detected.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, August 29th*, 1927.]

CCCLXXXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXII. An Attempt further to define the Probable Mechanism of Orientation in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD and FLORENCE RUTH SHAW.

RECENT studies of reactivity transmission have led to the recognition in aromatic substitutions of orienting effects originating in the following combinations of inductively propagated electronic strain (I,⟶) and tautomeric or electromeric transformations (T,↷) * (for summary see *Ann. Reports*, 1926, p. 129):

Type				
Symbol	(1) $+I$	(2) $-I$	(3) $-I+T$	(4) $+I+T$
Examples	Toluene.	Phenylammonium ions. Phenylsulphones.	Halogenobenzenes. Phenylthionium ions.	Phenoxide ion.

On the other hand, previous results provide little positive information with regard to the paths whereby the effects thus arising traverse the nucleus. It is possible that the inductive and the

* For reasons given elsewhere, the possible combinations represented by $+I-T$ and $-I-T$ will not here be separately discussed, and it is also unnecessary for our present purpose to consider superimposed polar orientation through space.

tautomeric disturbances travel by different routes and influence the reactivity in the various positions of the nucleus in different relative degrees. The one clearly established circumstance is that both types of disturbance affect primarily the ortho- and para-positions.

The paucity of information on this subject is partly due to the fact that a knowledge of the proportions in which isomerides are formed in substitutions furnishes only one of the two kinds of data which are necessary for an analysis of the influence of orienting groups on the reactivity in each nuclear position. The other, consisting of the relative velocities of the total substitutions ($o + m + p$) of different substances, is, in general, not available. In this paper, a preliminary analysis of certain cases is attempted with the aid of new experimental data.

Before proceeding to details, it is desirable to define the terms employed. By the phrase "the reactivity in a given nuclear position" is meant the velocity, relative to some standard, of the substitution which occurs in that position under the conditions of the comparison. The effect of an orienting group on the reactivity of each nuclear position may therefore be defined as the number of molecules substituted during a small element of time at the given nuclear carbon atom, divided by the number which would have been substituted during the same element of time at the same carbon atom had the orienting group been absent. This ratio may be termed the "coefficient of activation" (F) for the orienting group and the nuclear position considered.

The results recorded below refer to nitration. It is, of course, certain that the relative reactivities of different nuclear carbon atoms will be found to vary with the nature of the substitution studied (*e.g.*, nitration and mercuration). Nevertheless there are good grounds for the belief that the broad, qualitative conclusions (which alone it is desired to indicate in this preliminary communication) will be found to apply, without serious alteration, to the behaviour of the nucleus in a large class of substitution reactions.

Case 1. *Type* + I. *Example: Toluene.*—Toluene is nitrated to the extent of approximately 59% in its ortho-positions, 4% in its meta-positions, and 37% in its para-position. The disparity between the *op*-substitution on the one hand and *m*-substitution on the other is universally regarded as indicating the *op*-orienting tendency of the methyl group; but it may have arisen in various ways. For instance, the orienting group may have caused an increase in *op*-reactivity accompanied by a decrease of *m*-reactivity (alternation, in fact); or it may have given rise to an increase

op-reactivity, and left the *m*-position unaffected; or it may have produced a large increase in *op*-reactivity and a smaller increase in *m*-reactivity; and there are other possibilities. Actually each of the three alternatives mentioned has been assumed or implied in one or other of the theories of aromatic substitution which have been under discussion in recent years.

It is known from Wibaut's experiments (*Rec. trav. chim.*, 1915, **34**, 241) that toluene nitrates much more rapidly than benzene; but this does not decide the question at issue. Our study of the relative velocities of nitration of benzene and toluene has led to the conclusion that whilst the reactivity of each ortho- or para-carbon atom in toluene is increased roughly 30-fold, that of each meta-carbon atom is increased 2-fold by the directive action of the methyl group.

Benzene and toluene, both in excess, were nitrated together in a homogeneous solution; the reaction was allowed to proceed to completion and the product analysed. This method has an advantage over the alternative of carrying out parallel nitrations with benzene and toluene separately, inasmuch as uncertainties arising from imperfect, and consequently unequal, temperature control are avoided. The molecular ratio, R, in which the hydrocarbons are nitrated is not the ratio of the velocities, *ceteris paribus*, of the respective total substitutions, but may be used to determine it as follows.

It is assumed that the reactions are carried out in unit volume which does not change appreciably during the process. If x_0, y_0, and z_0 are the initial amounts of benzene, toluene, and nitric acid, respectively, and x and y are the quantities of benzene and toluene remaining after a time t, then at any moment

$$-dx/dt = k_x x\{x + y - (x_0 + y_0) + z_0\}$$

and

$$-dy/dt = k_y y\{x + y - (x_0 + y_0) + z_0\}.$$

These equations assume that the reactions are bimolecular and irreversible. This has been shown to be the case for the nitration of a considerable number of substances, including benzene, nitrobenzene, chlorobenzene, *op*-dinitrotoluene, and the three nitrobenzoic acids (Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79, 188, 364; 1901, **20**, 206, 352; Martinsen, *Z. physikal. Chem.*, 1905, **50**, 385; 1907, **59**, 605; Wibaut, *loc. cit.*). Phenol, however, is an exception, which is not surprising (Martinsen, *loc. cit.*; Klemenc, *Monatsh.*, 1914, **35**, 85; Arnall, J., 1923, **123**, 3111).

The above equations on simultaneous integration give

$$k_y/k_x = (\log y_\infty - \log y_0)/(\log x_\infty - \log x_0)$$

where x_∞ and y_∞ are the ultimate values of x and y, respectively. The two equations necessary to evaluate x_∞ and y_∞ are

$$x_\infty + y_\infty = x_0 + y_0 - z_0$$

and

$$R = (y_0 - y_\infty)/(x_0 - x_\infty),$$

and the final expression for the ratio of the velocities of the total substitutions is

$$\frac{k_y}{k_x} = \log\left\{1 - \frac{z_0}{y_0}\left(\frac{R}{1+R}\right)\right\} \Big/ \log\left\{1 - \frac{z_0}{x_0}\left(\frac{1}{1+R}\right)\right\}.$$

Naturally, the formula applies generally to the simultaneous nitration of pairs of aromatic substances, provided the assumptions made during its derivation are fulfilled. Even if they are not accurately fulfilled, the general conclusions still hold, for the replacement of k_y/k_x by R, which must in any case represent a too conservative estimate of the ratio of the speeds, leads to the same conclusions. If ω, μ, and π represent the proportions of the individual nitrotoluenes in the total nitrotoluenes produced, the respective coefficients of activation are

$$F_{\text{ortho}} = 3\omega k_y/k_x; \quad F_{\text{meta}} = 3\mu k_y/k_x \; ; \quad F_{\text{para}} = 6\pi k_y/k_x,$$

and on substituting the numerical data, we find

$$F_{\text{ortho}} = 27{\cdot}6 \; ; \quad F_{\text{para}} = 34{\cdot}6; \quad F_{\text{meta}} = 2{\cdot}1.$$

Case 2. *Type* — I. *Examples: Benzyltrimethylammonium Salts and Benzoic Acid.*—The examples mentioned have been chosen to represent this type (which includes all benzene derivatives in which *m*-substitution is known to predominate) because the first corresponds, we consider, with the simple inductive effect, whilst the second theoretically admits of a superimposed electromeric change, and might by some be considered as belonging more properly to one of the categories mentioned in the footnote on p. 2918.

The notoriously slower velocity of many *m*-oriented, as compared with the majority of *op*-oriented, substitutions, taken together with the observations of Martinsen (*loc. cit.*), who has shown, *inter alia*, that the introduction of a carboxyl, sulphonic acid, or nitro-group into a benzene derivative already containing one or more orienting groups diminishes the velocity of further substitution, leaves little doubt that in *m*-substitutions generally the *op*-positions escape an equivalent amount of attack owing to the deactivating influence of the directing substituent. Strictly, the point is unproved, but it is rendered sufficiently probable by the existing evidence to warrant its adoption as a working hypothesis. The question remains as to whether, either generally throughout the category, or in individual

cases, the *m*-position is activated, deactivated, or left unaffected. In certain examples in which a positive pole is attached to the nucleus the answer is clearly that the *m*-position, like the *op*-positions, is deactivated. For the substances mentioned in the head-line, we find that the coefficient of meta-activation is an extremely small fraction of unity, the *o*- and *p*-reactivity factors being smaller still, and we believe that this state of affairs is general amongst *m*-substituting benzene derivatives.

Case 3. *Type* $-\mathrm{I}+\mathrm{T}$. *Examples: The Halogenobenzenes, etc.*—This type includes the halogenobenzenes, the alkyl- and acyl-oxybenzenes, the acyl-, acyl-alkyl, and diacyl-aminobenzenes, nitrosobenzene, phenyl sulphoxides, phenylthionium salts, and all other compounds in which the atom attached to the ring attracts electrons more strongly than hydrogen ($-I$), but at the same time possesses unshared electrons which can be shared with the nucleus ($+T$).

In all the investigated instances, predominating *op*-substitution is the rule; but a substantial amount of simultaneous *m*-substitution is not theoretically impossible, since examples can be conceived in which the inductive process might effectively compete with tautomeric action. In the series of orienting groups NRR′, OR, I, Br, Cl, F (R = alkyl) the tautomeric effect diminishes and the inductive effect increases towards fluorine, but even in fluorobenzene the substitution is almost exclusively ortho-para. On the other hand, the velocity of substitution diminishes throughout the series to such an extent that the right-hand members become qualitatively differentiated from the left-hand members, and from the *op*-orienting groups, belonging to Case 1, which act by simple induction ($+I$). That is to say, the category under consideration provides examples of *op*-orienting groups which, unlike all other *op*-orienting groups, diminish the velocity of substitution: their coefficients of activation are fractional. In this respect they resemble the *m*-orienting groups of Case 2, but are distinguished from them by the fact that for the groups of Case 3 the meta-deactivation is even stronger than the *op*-deactivation, whereas the reverse holds for Case 2. From the left of the above series up to and including iodobenzene the values of k_y/k_x are greater than unity; for bromobenzene (0·2), chlorobenzene (0·01), and fluorobenzene (0·002) they are fractional, and the values given, although approximate, establish the order of the compounds.

The position assigned to the NHAc-group is based on nitration with a neutral reagent in a neutral or feebly acid medium (acetyl nitrate in acetic anhydride; Ingold and Ingold, J., 1926, 1310). The nitration of acetanilide with nitric acid in sulphuric acid as

solvent is interesting inasmuch as the same salt-forming process which absorbs the unshared electrons also charges, and enhances the electron affinity of the nitrogen atom, so that on increasing the strength of sulphuric acid the circumstances of Case 3 continuously approach those of Case 2; this takes place with corresponding changes in the coefficients of activation, which become fractional, and, as Noelting and Collins's experiments indicate, in the proportions of the isomerides (*Ber.*, 1884, **17**, 262).

Case 4. *Type* + I + T. *Example: The Phenoxide Ion.*—The general conditions affecting the substitution of the phenoxide ion are attested by known results. In particular, the high *op*-reactivity of the ion in comparison with undissociated phenol is well illustrated by the recent experiments of Soper and Smith (J., 1926, 1582).

Discussion and Conclusions.—Consideration of the facts summarised above has led us to the following conclusions:

(i) That whereas inductive effects of either sign operate primarily on the ortho- and para-positions, an appreciable second-order effect, always of the same sign as the primary effect, is relayed on to the meta-position.

(ii) That whereas tautomeric effects also operate powerfully on the ortho- and para-positions, no similarly appreciable second-order effect reaches the meta-position.

(iii) That whilst inductive effects give rise to an essentially permanent (not necessarily constant) molecular condition, the tautomeric effect (apart, possibly, from a small permanent residuum) is essentially temporary in character, assuming much greater importance at the moment of attack by a reagent than in the quiescent period preceding it.

Conclusion (i) is reached directly from the consideration of Cases 1 and 2. It implies that *m*-substitution in Case 1 arises from second-order *m*-activation, and in Case 2 from second-order *m*-deactivation, which explains the velocity relations. A consistent deduction is that, as *op*-deactivation increases, the proportion of the effect relayed to the *m*-position decreases, so that the *m*-directive power of a group (Case 2) runs *inversely* as the velocity of *m*-substitution. This is certainly true for a series such as CO_2H(80%), NO_2(93%), $\overset{+}{N}Me_3$(100% meta), in which the velocities rapidly diminish towards $\overset{+}{N}Me_3$ and the figures in brackets represent the proportion of meta-nitration.

Conclusion (ii) follows from Case 3. Considering the series (p. 2922) NRR′, OR, . . ., Cl, F, the term $-I$ may for many purposes be neglected in the left-hand members in comparison with $+T$, which produces strong *op*-activation but no *m*-activation which

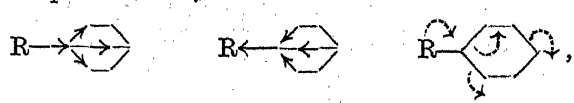
detectable in comparison. Again, if one imagines an extension of the series from NRR′ (*T* strong), through F (*T* weak), towards an extreme representative, such as $\overset{+}{\text{N}}$RR′R″, of Case 2,

$$\text{NRR}' \ldots \underset{\longleftarrow \text{increasing } -I \longrightarrow}{\overset{\longrightarrow \text{decreasing } T \longleftarrow}{(a) \ldots \text{F} \ldots (b)}} \ldots \overset{+}{\text{N}}\text{RR}'\text{R}''$$

the change over (*a*) from *op*-activation to *op*-deactivation occurs higher in the series than the change (*b*) from *op*- to *m*-substitution. For groups lying near the first of these critical positions (*a*) in the filled-in series, it is obvious that whilst the tautomeric effect can annul or reverse the strong *op*-deactivation arising from inductive action, it cannot reverse the relatively feeble *m*-deactivation. Indeed it seems to us that the condition of the whole group lying between the critical points (*a*) and (*b*) can be interpreted only along the lines indicated. The application to Case 4 is that appreciable *m*-substitution might arise if the inductive effect (+ *I*) were sufficiently powerful. Arnall's claim (J., 1924, **125**, 811) to have established 2—3% of *m*-substitution in the nitration of phenol might, if confirmed, be an indication in this direction. For systems of groups falling wholly within any one of Cases 1, 3 and 4, *op*-directive power must run parallel with the velocity of *op*-substitution, but no such simple rule can be laid down for the comparison of groups belonging to the different cases.

Conclusion (iii) is tentative, and is introduced because it appears necessary for the reconciliation of conclusions (i) and (ii). That inductive effects give rise to a permanent condition of electronic strain agrees with the known data relating to the molecular dipole moments of benzene derivatives, and it is consistent with our knowledge of reactivity transmission that a fractional part of charges arising on the ortho- and para-carbon atoms should be transmitted to the meta-carbon atom. On the other hand, it is difficult to see how *op*-charges which would be produced by the tautomeric effect can avoid similar transmission to the *m*-position, unless it be that they are "externally neutralised," that is, unless the electron displacements become large only at those moments when the reagent molecule which excites them is already committed to ortho- or para-attack.

The above interpretation, which is consistent with the following graphical representations,



is regarded as partly modifying, and partly giving definition to, the views originally expressed by Ingold and Ingold (*loc. cit.*), and as formulating in a more general way than has hitherto been possible the main principles which underlie the more recent communications from this laboratory on the subject of aromatic substitution. Only benzene substitutions are here dealt with, but the more important applications to naphthalene, quinoline, and certain other simple aromatic systems are sufficiently obvious. It will also be understood that the types discussed grade into one another, and in developing the work we shall investigate ω-halogenated and ω-carboxylated toluenes in order to emphasise this point.

Experimental.

Benzene was purified in the usual way. Toluene was purified by distillation, partial solidification (Ramsay), drying, and re-distillation (b. p. 110·4—110·8°). The other substances mentioned below were purified by distillation or crystallisation.

Toluene (1 mol.) and benzene (1 mol.) were nitrated together in a solution prepared from nitric acid (0·4 mol.) and acetic anhydride, the experiment being otherwise carried out as described by Holleman (*Rec. trav. chim.*, 1914, **33**, 1). Preliminary experiments had shown that for our purpose density determinations made with a moderately large pyknometer provided a more satisfactory method of analysis than measurements of refractive index. Accordingly, pure toluene was nitrated, without benzene, under the conditions indicated, and the mixed mononitro-derivatives were freed from unchanged toluene by distillation until the density remained constant. Mixtures of this product with similarly purified nitrobenzene had the following densities (d) at 25°; p denotes the percentage of nitrobenzene:

p	0·00	1·89	3·66	5·57	9·64	12·05	21·3	100·0
d	1·1526	1·1529	1·1537	1·1551	1·1566	1·1572	1·1616	1·1985

These points all lie on or close to the straight line represented by the equation $d = 1{\cdot}1526 + 0{\cdot}000459p$. The products of the mixed nitrations were likewise distilled to constant density to remove benzene and toluene, and the densities determined. They were d_{25}· 1·1555(i) and 1·1558(ii), which correspond with 6·3%(i) and 6·9%(ii) of nitrobenzene, that is, with 7·0(i) and 7·6(ii) molecules % of nitrobenzene. The agreement being apparently as good as could be expected from the method, the mean value, 7·3 molecules %, which gives $R_{Me} = 12{\cdot}7$, was used to calculate from the formula on p. 2921 that $k_y/k_x = 15{\cdot}7$. From this figure, by means of Holleman's data for the proportions of the isomerides (*loc. cit.*), the coefficients given in the introduction are obtained.

The investigation of the halogenobenzenes was carried out similarly with the following differences: (*a*) 1·0 mol. of nitric acid was used for the preparation of the acetyl nitrate solution, (*b*) the temperature of nitration was 45°, (*c*) the method of analysis was suited to the individual case. The product obtained from the experiments with fluorobenzene was distilled to remove unchanged benzene and fluorobenzene, and the remaining binary mixture hydrolysed with boiling sodium hydroxide solution to remove the fluorine as fluoride ion from the nitrofluorobenzenes—a process which is quantitative. The products obtained from chlorobenzene and bromobenzene were distilled to remove benzene, and the remaining ternary mixtures were hydrolysed under conditions known to be appropriate in each case. The liberated halide ions were estimated, and the residual binary mixtures insoluble in alkali submitted to ultimate analysis. By means of these methods, concordant determinations gave the following values: $R_F = 0{\cdot}0107$, $R_{Cl} = 0{\cdot}027$, $R_{Br} = 0{\cdot}36$, whence the figures given in the introduction were calculated. Competitive nitration of benzene and iodobenzene gave iodonitrobenzenes exclusively (R_I large), and anisole behaved similarly.

Since the medium used in the above experiments does not dissolve benzyltrimethylammonium picrate or benzoic acid sufficiently, a mixture of pure acetic acid and sulphuric acid in equimolecular proportion (15 mols. of each) was used as solvent for the nitration of these substances. The temperature was 0°. In each case, the benzene alone was nitrated and the other substance was recovered pure and unaccompanied by any trace of its nitro-derivatives; this was proved by m. p. and mixed m. p., and, for benzoic acid, confirmed by sublimation. In the course of the nitration of benzyltrimethylammonium picrate, picric acid separated from solution, but we do not regard this as invalidating the experiment, since the benzyltrimethylammonium ion remained dissolved.

The nitration of acetanilide was similarly investigated with identical results.

THE UNIVERSITY, LEEDS. [*Received, October 28th*, 1927.]

CCCLXXXIX.—*Melting Points of the Substituted Amides of Dibasic Acids.*

By CUTHBERT RICHMOND BARNICOAT.

THE members of homologous series usually show a fairly regular variation in physical properties as each series is ascended. The mono- and the di-basic acids are exceptions, as their melting points

rise and fall alternately. Biach (*Z. Physik*, 1904, **50**, 43) pointed out that this alternation is really quite general, as it appears in at least sixteen series of compounds. By plotting the melting points against the number of carbon atoms in the chain, two distinct curves, not necessarily exhibiting rise and fall, are obtained in each case, and those compounds containing an even number of carbon atoms lie on the higher curve. This phenomenon, evident even in the paraffins, appears to be due to something inherent in the carbon chain itself.

Robertson (J., 1908, **93**, 1033; 1919, **115**, 1210) has shown that the amides and substituted amides of the monobasic fatty acids exhibit this irregularity to an even more marked extent than the acids themselves. The investigations did not extend to dibasic acids, and it is to the study of the corresponding compounds of these that this work is confined.

EXPERIMENTAL.

The method of preparation of these substances was much the same as that described in Robertson's papers (*loc. cit.*).

The acids were from Kahlbaum, except the three highest members which were prepared by Lumsden and Walker's method (J., 1901, **79**, 1191).

All the melting-point determinations were made by the capillary-tube method in a castor-oil bath, and are uncorrected. The same standardised thermometer was used throughout.

The compounds not containing bromine were analysed by Kjeldahl's method, and the bromo-derivatives by the chromic acid method (Robertson, J., 1915, **107**, 902).

In Table I are the redetermined values of the melting points of compounds which were already known.

TABLE I.

Compound.	Formula.	M. p.	Previous observers.
Malonanilide	$C_{15}H_{14}O_2N_2$	224°	225°, 230°
Malono-*o*-toluidide	$C_{17}H_{18}O_2N_2$	189	193
Malono-*p*-toluidide	$C_{17}H_{18}O_2N_2$	247	248, 250
Succinanilide	$C_{16}H_{16}O_2N_2$	227	226
Succino-*p*-toluidide	$C_{18}H_{20}O_2N_2$	260	256
Succino-*o*-toluidide	$C_{18}H_{20}O_2N_2$	231	100 *
Glutaranilide	$C_{17}H_{18}O_2N_2$	223	223, 214
Adipanilide	$C_{18}H_{20}O_2N_2$	235	235, 233, 240
Pimelanilide	$C_{19}H_{22}O_2N_2$	152	155
Suberanilide	$C_{20}H_{24}O_2N_2$	182	183, 187
Subero-*p*-toluidide	$C_{22}H_{28}O_2N_2$	219	218
Azelanilide	$C_{21}H_{26}O_2N_2$	184	185
Sebacanilide	$C_{22}H_{28}O_2N_2$	200	198

* This is probably the melting point of succino-*o*-toluidic acid.

In Table II are the m. p.'s and analyses of the new compounds prepared in connexion with this work.

TABLE II.

Compound.	Formula.	M. p.	% N found.	% N calc.
n-Nonanedicarboxyamide	$C_{11}H_{22}O_2N_2$	173°	12·8	13·1
n-Decanedicarboxyamide	$C_{12}H_{24}O_2N_2$	189	12·0	12·3
n-Nonanedicarboxyanilide	$C_{23}H_{30}O_2N_2$	156	7·45	7·65
n-Decanedicarboxyanilide	$C_{24}H_{32}O_2N_2$	191	7·3	7·4
n-Undecanedicarboxyanilide	$C_{25}H_{34}O_2N_2$	158	7·0	7·1
Glutaro-*o*-toluidide	$C_{19}H_{22}O_2N_2$	222	9·2	9·0
Adipo-*o*-toluidide	$C_{20}H_{24}O_2N_2$	222	8·2	8·6
Pimelo-*o*-toluidide	$C_{21}H_{26}O_2N_2$	174	8·2	8·3
Subero-*o*-toluidide	$C_{22}H_{28}O_2N_2$	185	7·8	7·9
Azelo-*o*-toluidide	$C_{23}H_{30}O_2N_2$	171	7·6	7·65
Sebaco-*o*-toluidide	$C_{24}H_{32}O_2N_2$	179	7·5	7·4
n-Nonanedicarboxy-*o*-toluidide ...	$C_{25}H_{34}O_2N_2$	164	7·0	7·1
n-Decanedicarboxy-*o*-toluidide ...	$C_{26}H_{36}O_2N_2$	164	7·2	6·9
n-Undecanedicarboxy-*o*-toluidide	$C_{27}H_{38}O_2N_2$	142	6·7	6·6
Glutaro-*p*-toluidide	$C_{19}H_{22}O_2N_2$	218	8·7	9·0
Adipo-*p*-toluidide	$C_{20}H_{24}O_2N_2$	241	8·3	8·6
Pimelo-*p*-toluidide	$C_{21}H_{26}O_2N_2$	206	8·2	8·3
Azelo-*p*-toluidide	$C_{23}H_{30}O_2N_2$	198	7·5	7·65
Sebaco-*p*-toluidide	$C_{24}H_{32}O_2N_2$	201	7·2	7·4
n-Nonanedicarboxy-*p*-toluidide ...	$C_{25}H_{34}O_2N_2$	191	7·4	7·1
n-Decanedicarboxy-*p*-toluidide ...	$C_{26}H_{36}O_2N_2$	165	7·0	6·9
n-Undecanedicarboxy-*p*-toluidide	$C_{27}H_{38}O_2N_2$	156	6·5	6·6

In Table III are the m. p.'s and analyses of the new bromo compounds.

TABLE III.

Compound.	Formula.	M. p.	% Br found.	% Br calc.
Succino-*p*-bromoanilide	$C_{16}H_{14}O_2N_2Br_2$	284°	37·4	37·5
Glutaro-*p*-bromoanilide	$C_{17}H_{16}O_2N_2Br_2$	256	36·6	36·4
Adipo-*p*-bromoanilide	$C_{18}H_{18}O_2N_2Br_2$	268	35·5	35·3
Pimelo-*p*-bromoanilide	$C_{19}H_{20}O_2N_2Br_2$	240	34·3	34·1
Subero-*p*-bromoanilide	$C_{20}H_{22}O_2N_2Br_2$	248	33·0	33·2
Azelo-*p*-bromoanilide	$C_{21}H_{24}O_2N_2Br_2$	225	32·1	32·3
Sebaco-*p*-bromoanilide	$C_{22}H_{26}O_2N_2Br_2$	225	31·1	31·4
n-Nonanedicarboxy-*p*-bromoanilide	$C_{23}H_{28}O_2N_2Br_2$	215	30·5	30·5
n-Decanedicarboxy-*p*-bromoanilide ...	$C_{24}H_{30}O_2N_2Br_2$	213	29·5	29·7
n-Undecanedicarboxy-*p*-bromoanilide	$C_{25}H_{32}O_2N_2Br_2$	202	28·9	29·0

Remarks.—Acids. The differences in melting point of adjacent members are considerably greater than those between the corresponding monobasic acids, and the two curves tend to converge. A minimum is obtained at the fifth member (Fig. 1).

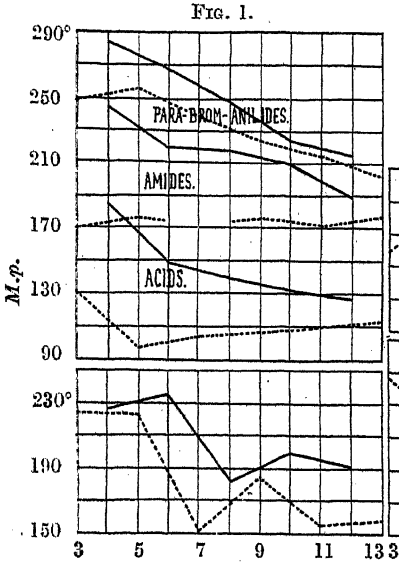
Amides. The curves resemble those of the acids, as the terminal groups are somewhat similar. The melting points are on the average 70° higher, and the differences between corresponding members more marked (Fig. 1).

Anilides. The introduction of a phenyl group causes a striking change in the nature of the curves (Fig. 2), that of the odd series

showing greater irregularity than its fellow, and less marked alternation results (*i.e.*, the curves lie closer together). Alternation appears to exhibit an unusual arrangement in fours.

o-*Toluidides* (Fig. 3). There is a marked similarity between these and the two following series, with substituted phenyl groups in the chain. A pronounced maximum is attained at the fifth member. The relative variation between the odd and the even series decreases slightly. The initial irregularity is apparently due to the unsymmetrical arrangement of the *o*-tolyl ring distorting

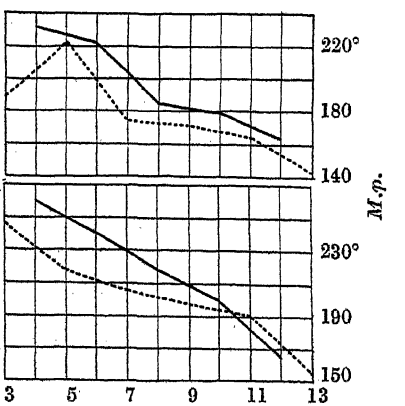
FIG. 1.



Number of carbon atoms in chain.

FIG. 2. *Anilides.*

FIG. 3. o-*Toluidides.*



Number of carbon atoms in chain.

FIG. 4. p-*Toluidides.*

the molecule, particularly when the chain is short and the end groups are in close proximity.

p-*Toluidides* (Fig. 4). The curves show slightly greater variation and the molecule is symmetrical, causing irregularity to be absent.

p-*Bromoanilides* (Fig. 1). The bromine atom has the most marked influence of all the substituents, producing curves almost devoid of irregularity.

I wish to thank Professor P. W. Robertson for his advice and for the interest he has taken in this work.

VICTORIA UNIVERSITY COLLEGE,
WELLINGTON, NEW ZEALAND.

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CCCXC.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part III. Some Reactions of Thionylalizarin.*

By ALBERT GREEN.

SINCE thionylalizarin appears to be the most reactive of the thionyl compounds previously examined (J., 1924, **125**, 1450; 1926, 2198; this vol., pp. 500, 554, 2341), a further study of its reactions has been carried out.

It is now shown that although the interaction between the thionyl compound and *weak* organic acids provides a general method of preparing the corresponding 2-acyl derivatives of alizarin, yet with the stronger organic acids the thionyl derivative reverts to alizarin. The following acids yield 2-monoacyl derivatives: acetic (*loc. cit.*), phenylacetic, phenoxyacetic, cinnamic, benzoic, *o*-toluic, *m*-bromobenzoic, and *p*-bromobenzoic. Monochloroacetic acid gives a mixture of alizarin and a substance having the appearance of its monochloroacetate, whilst with dichloroacetic, trichloroacetic, and dibromoacetic acids thionylalizarin gives alizarin only.

It is thus clear that the reaction which a thionyl compound undergoes with an organic acid depends on the nature of that acid. The nature of the thionyl compound is also a factor, for while the thionyl derivatives of alizarin and of pyrocatechol are quantitatively converted into their monoacetates (*loc. cit.*) by acetic acid, yet under the same conditions thionylhystazarin (*loc. cit.*) gives hystazarin only.

Diacyl derivatives are obtained by the action of benzoic anhydride, benzoyl chloride and acetyl chloride, but succinic and phthalic anhydrides react neither with thionylalizarin nor with alizarin itself. This may be accounted for by the fact that the production of alizarin succinate (or phthalate) would necessitate the formation of a cyclic structure of eight atoms. Dibenzoylalizarin has been obtained in two crystalline modifications, melting at 160° (labile) and at 187° respectively.

The thionyl compound is rapidly decomposed, with evolution of sulphur dioxide, by boiling absolute ethyl alcohol and by hot phenol and in both cases the products are pure alizarin.

In attempts to prepare ethers by the condensation of thionylalizarin with alkyl halides and with alkyl sulphates no reaction was observed.

Thionylalizarin reacts readily with hot primary aromatic amines, with evolution of sulphur dioxide, to give alizarin, which then undergoes further slow reaction with the bases to yield secondary

amines. For example, in one experiment, the product obtained after boiling thionylalizarin in dry aniline for 1 hour contained less than 1% of nitrogen, gave the reactions of alizarin and melted at 265—268°. This melting point was raised to 275—277° by admixture with pure alizarin. Similar results were obtained with other aromatic amines, and the reaction was not investigated further.

EXPERIMENTAL.

Interaction of Thionylalizarin with Acids, Acid Anhydrides, and Acid Chlorides.—Methods. A. In the case of the lower-melting acids, a slight excess was heated with thionylalizarin at 150—170°. When the evolution of sulphur dioxide was no longer vigorous (usually 10 to 15 minutes), the melt was allowed to cool, boiled with ether to remove any unchanged acid, and the residue was recrystallised from benzene or absolute alcohol. Yields of 90 to 95% of the pure products were obtained.

B. The acid or anhydride and thionylalizarin were heated in dry nitrobenzene at 170° for 40 to 60 minutes. On cooling, a portion of the product usually crystallised. A further quantity was obtained by adding ether to the solution and allowing it to stand. The yields averaged 60%.

C. Benzoyl chloride reacted vigorously at its boiling point with thionylalizarin, and dibenzoylalizarin, m. p. 187°, crystallised on cooling. With acetyl chloride no reaction was observed after 4 hours' boiling, but when the substances were heated in a sealed tube at 150—170° for 2 hours, diacetylalizarin was obtained in 80% yield.

Alizarin benzoates. 2-Monobenzoylalizarin (methods *A* and *B*) was obtained from absolute alcohol in small, chrome-coloured needles, m. p. 208—210° (D.R.-P. 297,261 gives 214—216°). When mixed with a specimen prepared from alizarin and the theoretical amount of benzoyl chloride in pyridine solution, it showed the same m. p. (Found: C, 73·3; H, 3·6. Calc. for $C_{21}H_{12}O_5$: C, 73·3; H, 3·5%).

Dibenzoylalizarin (*B* and *C*). When prepared from the thionyl compound and benzoic anhydride in nitrobenzene solution, *dibenzoylalizarin* separated in clusters of small, pale chrome crystals, m. p. 160°, which was unchanged by further immediate crystallisation from benzene (Found: C, 74·8; H, 3·7. $C_{28}H_{16}O_6$ requires C, 75·0; H, 3·6%). This labile form, on being kept for a week in contact with a little of the original nitrobenzene solution, was transformed to the stable modification, which consisted of stout, primrose prisms, m. p. 187° (Found: C, 74·9; H, 3·7%) (compare Barnett and Cook, J., 1922, **121**, 1389). Other preparations of this derivative from

alizarin and benzoyl chloride in pyridine gave the higher-melting form.

The following 2-*monoacyl* derivatives of alizarin were also prepared. The methods of preparation are indicated, and the calculated values for C, H, and Br are given in brackets after the found values.

2-Acyl derivatives of alizarin.	Appearance and m. p.	Recrystallisation solvent and analyses.
Phenylacetyl (*A*) ...	Greenish-yellow needles, m. p. 165°.	Benzene. 73·7; 4·0 (73·7; 3·9).
Phenoxyacetyl (*A*) ...	Small, yellow needles, m. p. 179°.	Benzene. 70·7; 3·7 (70·6; 3·7).
Cinnamoyl (*A* and *B*)	Golden-yellow prisms, m. p. 209°.	Benzene. 74·5; 3·7 (74·6; 3·8).
o-*Toluoyl* (*A*)	Fine, ochre needles, m. p. 192°.	Benzene or absolute alcohol. 73·7; 3·9 (73·7; 3·9).
m-*Bromobenzoyl* (*A*)	Small, greenish-yellow needles, m. p. 214°.	Toluene. Br, 18·7 (18·9).
p-*Bromobenzoyl* (*B*)	Greenish-yellow needles, m. p. 195°.	Benzene. Br, 18·9 (18·9).

Condensations with Halogen-substituted Acetic Acids.—(1) *Monochloroacetic acid.* Thionylalizarin (2 g.) was treated with the carefully purified acid, according to method *A*. The product, crystallised from benzene, consisted of 1·6 g. of an intimate mixture of fine, yellow needles, which closely resembled the monoacyl compounds previously examined, and of fine, reddish-brown flakes. The mixture contained 5·8% of chlorine (the monochloroacetate requires 11·2%). Similar results were obtained by varying the experimental conditions. After repeated extraction of the mixtures with light petroleum, a residue of pure alizarin was obtained; m. p. 288°, either alone or mixed with an authentic specimen.

(2) Thoroughly dried and purified dichloro-, trichloro-, and dibromo-acetic acids in all experiments gave theoretical yields of halogen-free alizarin, which was identified by mixed melting-point determinations with the pure substance, and by conversion into the diacetate.

The products from alcoholic and phenolic solutions of thionylalizarin were shown to be alizarin in the same manner.

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THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, September 3rd*, 1927.]

CCCXCI.—*The Isomerism of the Oximes. Part XXXII. Sulphates.*

By Oscar L. Brady and Alan D. Whitehead.

Luxmoore (J., 1896, **69**, 180) showed that α-benzaldoxime could be converted into the β-isomeride by means of concentrated sulphuric acid and isolated both the α- and the β-benzaldoxime sulphate, $C_6H_5{\cdot}CH{:}NOH,H_2SO_4$. The α-oxime sulphate regenerated the α-oxime on decomposition with aqueous ammonia at 0°, and on keeping rapidly changed to the β-oxime sulphate; this gave the β-oxime on treatment with alkalis. A number of other aromatic aldoxime sulphates have now been prepared and Luxmoore's method of converting the α- into the β-oxime has been investigated in the hope that it would prove more convenient than the usual procedure through the hydrochloride. Further, it was thought that it might be possible, through the sulphate, to bring about isomeric change in those oximes which do not form hydrochlorides (Brady and Dunn, J., 1915, **107**, 1862; Brady and Manjunath, J., 1924, **125**, 1068).

When α- *o*-, *m*-, or *p*-nitro- or α-*p*-methoxy-benzaldoxime is dissolved in concentrated sulphuric acid, the sulphate of the α-oxime is first formed, and the solution on neutralisation with sodium carbonate regenerates the α-oxime; if the solution be kept for some time or heated to 100°, or if the temperature rises too much during the dissolution owing to the heat of reaction, the sulphate of the β-oxime is produced, and the solution on neutralisation gives the β-oxime. Provided that the temperature is kept low, the dry sulphates of these oximes, isolated by various means from the freshly prepared solutions, consist mainly of the α-form, differing in this respect from the hydrochlorides, since, although the α-hydrochloride of *p*-methoxybenzaldoxime can be obtained at — 10°, those of *m*- and *p*-nitrobenzaldoxime are stable only at very low temperatures (Brady and Dunn, J., 1916, **109**, 680; 1923, **123**, 1798). The solid sulphate from benzaldoxime consisted of the β-form (compare Luxmoore, *loc. cit.*). In the case of α-*o*-methoxybenzaldoxime, which cannot be converted into the β-isomeride through the hydrochloride, sulphate formation likewise failed to bring about the change; α-*o*-chlorobenzaldoxime, which yields the β-form only with difficulty through the hydrochloride, gave only an α-sulphate; 3 : 4-methylenedioxybenzaldoxime gave an α-sulphate which could not be converted into the β-form owing to decomposition of the methylene group on heating or keeping. α-6-Nitro-3 : 4-methylenedioxybenzaldoxime and α-6-bromo-3 : 4-dimethoxybenzaldoxime

which do not form hydrochlorides, gave α-sulphates, but these compounds did not change to the β-forms.

When solutions of α-benzaldoxime, *o*-, *m*-, and *p*-nitro-, and *p*-methoxy-benzaldoximes in concentrated sulphuric acid were heated for a short time at 100°, cooled, and poured into a large excess of sodium carbonate solution, products were obtained which on crystallisation gave fairly satisfactory yields of the β-oximes. This method is probably the quickest way of preparing small amounts of the β-oximes, but does not work well with quantities much above 2 grams; it seems that owing to the longer time required for neutralisation when larger quantities are used, as in the case of the hydrochlorides, partial reversion of the β- to the α-oxime takes place.

Prolonged heating of aldoximes with concentrated sulphuric acid results in the formation of the corresponding amides. It is impossible to decide at present whether this is a Beckmann change (I) or dehydration to nitrile followed by addition of water in another way (II), since the nitrile on similar treatment yields the amide.

$$\mathrm{R{\cdot}\overset{|}{C}O{-}NH_2} \longleftarrow \mathrm{R{\cdot}\overset{||}{C}{\cdot}OH{-}HN} \longleftarrow \mathrm{R{\cdot}\overset{||}{C}H{-}HO{\cdot}N} \longrightarrow \mathrm{RCN} \longrightarrow \mathrm{R{\cdot}CO{\cdot}NH_2}$$

(I.) (II.)

o-Nitro-, *o*-methoxy-, 3 : 4-methylenedioxy-, and 6-nitro-3 : 4-methylenedioxy-benzaldoxime undergo extensive charring on heating with sulphuric acid and could not be investigated under such conditions.

Experimental.

α-Benzaldoxime.—Formation of β-oxime. The method of converting the α- into the β-oxime by means of sulphuric acid has been investigated in order to find the best conditions. When benzaldoxime was dissolved in 96% sulphuric acid (5 g.) the temperature rose to 40—50° and after 4·5 g. of oxime had been added the solution became thick with crystals of benzaldoxime sulphate. If the solid sulphate was separated from the acid, pressed on a porous tile, and added to excess of 2*N*-sodium carbonate, fairly pure β-oxime was obtained, but when the whole semi-solid material was slowly stirred into a volume of 2*N*-sodium carbonate containing 4 mols. of carbonate for each mol. of acid used (this will subsequently be referred to as neutralisation), an oil separated consisting of a mixture of β- and unchanged α-oxime. With 5 g. of oxime and 10 g. of acid, complete solution was attained, but neutralisation gave a waxy product still containing much α-oxime. When a solution of 5 g. of oxime in 20 g. of acid was kept for a month in a closed flask, or when a

solution of 1 g. of oxime in 5 g. of acid was heated on the water-bath for 30 minutes, the product obtained yielded on neutralisation a fairly pure β-oxime (m. p. 108—111°), one crystallisation from benzene giving the pure compound.

Formation of benzamide. A solution of α-benzaldoxime (5 g.) in concentrated sulphuric acid (15 g.) was heated on the water-bath for 12 hours, kept for 2 days, and neutralised, a white precipitate being obtained. The suspension was extracted with ether and then with chloroform. The ethereal solution contained impure β-benzaldoxime (identified by comparison with an authentic specimen and by conversion into the α-benzoyl derivative; the yield was 14% of the oxime taken), no aldehyde or nitrile, and 1·42 g. of benzamide; 1 g. of benzamide was obtained from the chloroform extract, the total yield being approximately 50% of the oxime taken. The aqueous solution, after being acidified with hydrochloric acid, yielded to ether 0·6 g. of benzoic acid, corresponding to 12% of the oxime employed. Of the 24% of the oxime unaccounted for, most was probably lost during manipulation, some possibly as sulphonate.

α-m-*Nitrobenzaldoxime.*—When the oxime (1 g.) was stirred into sulphuric acid (2 g.), the temperature rose to 35°. The almost colourless, viscous solution was cooled in a desiccator for 30 minutes and poured into dry ether. The precipitated α-m-*nitrobenzaldoxime sulphate* was collected, washed rapidly twice with dry ether, and kept for 12 hours in an evacuated desiccator. It consisted of a white, crystalline powder, m. p. 71—76°, and was analysed by decomposition of a weighed amount with water and titration of the sulphuric acid with *N*/10-sodium carbonate and methyl-orange (Found: H_2SO_4, 41·2. $C_7H_6O_3N_2,H_2SO_4$ requires H_2SO_4, 37·1%). The freshly prepared solid sulphate on decomposition with 2*N*-sodium carbonate regenerated the α-oxime.

When α-*m*-nitrobenzaldoxime (2 g.) was dissolved in sulphuric acid (10 g.), and the solution neutralised at once, a product, m. p. 107°, was obtained which was almost pure α-oxime. If the solution was kept for 24 hours before being neutralised, the recovered oxime melted at 75°, indicating that about 50% conversion had occurred; whilst if the solution was heated on the water-bath for 30 minutes and then neutralised, a fairly pure β-oxime was obtained which gave a good yield of pure β-*m*-nitrobenzaldoxime after one crystallisation from benzene.

α-*m*-Nitrobenzaldoxime (5 g.) was dissolved in sulphuric acid (15 g.) and heated for 7 hours on the water-bath. On neutralisation of the clear brown solution an oil separated which soon solidified.

The whole was extracted once with ether, the undissolved solid was collected and dissolved in hot chloroform, and the aqueous layer also was extracted with chloroform. The ethereal solution was extracted twice with 2*N*-sodium hydroxide, and then with a solution of hydroxylamine hydrochloride in excess of 2*N*-sodium hydroxide to remove aldehyde as the sodium salt of the oxime; the aqueous layer in the latter case was but faintly coloured, indicating that little aldehyde was present. The ether on evaporation yielded 0·8 g. of somewhat impure *m*-nitrobenzamide, one crystallisation from water giving the pure product. The sodium hydroxide extracts were saturated with carbon dioxide and the precipitated oxime was extracted with ether, 2·1 g. of a mixture of α- and β-oximes being obtained (the time of manipulation would account for some conversion of β- into α-oxime); crystallisation from water, containing a little hydrochloric acid to convert the β- into the α-oxime, yielded pure α-*m*-nitrobenzaldoxime. The combined chloroform solutions were extracted with 2*N*-sodium hydroxide and the faintly coloured alkaline solution was added to those obtained from the ethereal extract. The chloroform on evaporation gave 0·5 g. of *m*-nitrobenzamide.

m-Nitrobenzonitrile (2 g.) was heated with sulphuric acid (6 g.) for 7 hours; some charring occurred due probably to the presence of a little of the *o*-nitro-compound. On neutralisation a dark solid was precipitated which, after crystallisation from water (animal charcoal), gave more than 1 g. of pure *m*-nitrobenzamide.

m-Nitrobenzamide often crystallises with water of crystallisation and must be kept in a desiccator for 12 hours before its melting point is taken. A specimen, crystallised from hot water with rapid cooling and dried rapidly by pressing on several porous tiles, collapsed in a melting-point tube when this was put into a bath at 105°, but it did not melt until 141°. On being kept in a desiccator, it lost 12·4% of its weight (calc. for $1H_2O$, 9·8%); the high result is due to the difficulty of freeing the compound from extraneous moisture.

The following sulphates were prepared by analogous methods, and the products of their decomposition investigated as before. The results are described in the introduction. The compounds consist, unless otherwise stated, of white microcrystalline powders. α-o-*Methoxybenzaldoxime sulphate* (1 g. of oxime; 4 g. of acid), m. p. 143° (Found: H_2SO_4, 38·3. $C_8H_9O_2N,H_2SO_4$ requires H_2SO_4, 39·3%). α-o-*Chlorobenzaldoxime sulphate* (1 g. of oxime; 1 g. of acid) (Found: H_2SO_4, 36·9. C_7H_6ONCl,H_2SO_4 requires H_2SO_4, 38·6%). α-6-*Bromo*-3 : 4-*dimethoxybenzaldoxime sulphate* (1 g. of

oxime; 2 g. of acid), a canary-yellow, granular solid, m. p. 105° (Found: H_2SO_4, 27·7. $C_9H_{10}O_3NBr,H_2SO_4$ requires H_2SO_4, 27·3%). α-6-*Nitro*-3 : 4-*methylenedioxybenzaldoxime sulphate* (1 g. of oxime; 1 g. of acid), a brown powder, m. p. 110—135°, readily dissociating into oxime and acid in the presence of ether or on exposure to moist air (Found: H_2SO_4, 31·1. $C_8H_6O_5N_2,H_2SO_4$ requires H_2SO_4, 31·8%). p-*Nitrobenzaldoxime sulphate*, a light fawn, granular solid too deliquescent for a melting point to be obtained (Found: H_2SO_4, 38·6. $C_7H_6O_3N_2,H_2SO_4$ requires H_2SO_4, 37·1%). This compound dissociates very easily and is difficult to obtain; it was prepared by adding the oxime (1·5 g.) to sulphuric acid (1 g.) until the mixture began to crystallise; the pasty mass was stirred into ether, rapidly collected, and washed once only with dry ether. No solid sulphate could be obtained from *o*-nitrobenzaldoxime, only a very small amount of oil being precipitated from the sulphuric acid solution by ether. α-3:4-*Methylenedioxybenzaldoxime sulphate* (Found: H_2SO_4, 37·6. $C_8H_7O_3N,H_2SO_4$ requires H_2SO_4, 37·2%) was obtained by stirring the oxime (2·5 g.) into acid (2 g.) warmed to 60°, cooling, collecting the solid which separated, and washing it with dry ether. α-p-*Methoxybenzaldoxime sulphate* (2 g. of oxime; 10 g. of acid), m. p. 79—80° (Found: H_2SO_4, 38·9. $C_8H_9O_2N,H_2SO_4$ requires H_2SO_4, 39·3%).

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, September 14th*, 1927.]

CCCXCII.—*Properties of Conjugated Compounds. Part III. The Bearing of Hexatriene Chemistry on the Reactive Form of Conjugated Hydrocarbons.*

By ERNEST HAROLD FARMER, BANARSI DAS LAROIA, THEODORE MACLEAN SWITZ, and JOCELYN FIELD THORPE.

THE chemistry of hexatriene is of fundamental importance from two standpoints. First, although a simple conjugated hydrocarbon, its additive behaviour is at variance, according to van Romburgh's observation, with the requirements of the Thiele hypothesis, and secondly its structure allows the anticipation of two geometrical isomerides, one of which, approaching so closely the Kekulé representation of benzene, has been a subject of speculation in respect of a possible valency connexion between the terminal carbon atoms.

With van Romburgh's hexatriene the evidence for 3 : 4-addition

is, apparently, convincing. The formation of the hydrocarbon from Griner's *s*-divinylglycol (I) (the reduction product of acraldehyde, *Ann. Chim. Phys.*, 1892, **26**, 368) through the 3 : 4-dibromide (II)

$\begin{matrix}CH(OH)\cdot CH{:}CH_2\\ CH(OH)\cdot CH{:}CH_2\end{matrix}$	$\begin{matrix}CHBr\cdot CH{:}CH_2\\ CHBr\cdot CH{:}CH_2\end{matrix}$	$\begin{matrix}CH\cdot CH{:}CHPh\\ CH\cdot CH{:}CHPh\end{matrix}$
(I.)	(II.)	(III.)

would appear quite normal; further the crystalline product obtained by adding bromine to the hydrocarbon, since it is identical with the parent dibromide (II), would be naturally regarded as a 3 : 4-dibromide. At the outset of this investigation this series of reactions appeared to offer an attractive method for testing the generality of the 3 : 4-additive mode in the hexatriene series. Thus it was found with a 1 : 6-diphenylhexatriene (III) synthesised from cinnamaldehyde through stages analogous to (I) and (II), that out of the very numerous geometrical, stereo-, and position isomerides theoretically possible the additive dibromide actually obtained was identical with the parent dibromide; with 1 : 6-dimethylhexatriene and 2 : 5-dimethyl-1 : 6-diethylhexatriene, which were also synthesised, polymerisation took place too rapidly to allow of satisfactory bromination.

Derivation of Hexatriene Bromides.

Re-examination of the *s*-divinylglycol from acraldehyde showed that, contrary to Griner's opinion, it was a mixture of *meso* and *racemic* forms: on reduction, it yielded two forms of *s*-diethylglycol, each oxidisable to propionic acid. On replacement of hydroxyl by bromine with phosphorus tribromide under Griner's conditions—conditions under which much hydrogen bromide was liberated—the product, so far from being homogeneous, consisted of solid and liquid bromides boiling over a considerable range. Excluding the highest-boiling fraction consisting of a tribromohexene (the formation of which was reduced to a minimum by modifying Griner's method), the material consisted of a liquid and a solid, designated for convenience (A) and (B). Of these, the solid (B) was the compound utilised by van Romburgh for generating hexatriene, whilst (A), an impure liquid dibromide, undoubtedly suffered progressive conversion into the isomeride (B), the active agent in the conversion being in all probability the hydrogen bromide liberated during distillation. Although in purifying this unstable substance repeated fractionation involving considerable loss of material was necessary, large quantities of it were prepared. On treatment with zinc it yielded a new hydrocarbon closely approach-

ing van Romburgh's compound in physical properties and superficially indistinguishable therefrom. Whereas the new hydrocarbon yielded an oily dibromide (C) (by far the most stable of the liquid dibromohexadienes encountered) and on further bromination an oily tetrabromide, the dibromide and tetrabromides (two) from van Romburgh's hydrocarbon were all crystalline.

To this second hydrocarbon, differing entirely in its additive bromides from dihydrobenzene, must be attributed the hexatriene structure, the only feasible relationship with the known hexatriene being one of *cis-trans* isomerism as in (IV) and (V).

(IV.) $CH_2{:}CH{\cdot}CH$ ‖ $HC{\cdot}CH{:}CH_2$ $\qquad$ $HC{\cdot}CH{:}CH_2$ ‖ $HC{\cdot}CH{:}CH_2$ (V.)

The different chemical behaviour of these substances was discovered at a very early stage, but trustworthy evidence as to which was the *trans-* and which the *cis*-form was difficult to secure. A series of oxidations undertaken in the hope of retaining the $\gamma\delta$-carbon atoms in recognisable products such as maleic or tartaric acid proved fruitless. Attention was therefore centred on the dibromides (A), (B), and (C), structural discrimination between which represented the only apparent approach towards the elucidation of hexatriene chemistry. Of hexatriene dibromides which demand consideration, there are, excluding improbable 1 : 3-, 2 : 4-, and 2 : 5-forms, seven structures (geometrical, stereo-, and position isomerides) theoretically derivable from *trans*-hexatriene and an additional one from *cis*-hexatriene. Here again in the assignation of formulæ, direct oxidation methods had to be abandoned; some thirty oxidations of the various dibromides with different reagents were carried out and, except in one important particular mentioned later, yielded little useful information.

Structural Relationship of Hexatriene Dibromides.

Griner had observed that the solid dibromide (B) gave a diethoxyhexadiene with alcoholic potash. This conversion was found to be almost quantitative when sodium ethoxide was used, and the homogeneous product had the advantage, unusual in this series, of considerable stability. On catalytic hydrogenation it yielded diethoxyhexane, which was successively convertible by usual processes into di-iodohexane, dicyanohexane, and a dibasic acid. The last proved to be suberic acid, indicating that the substituents at each stage occupied the 1 : 6-positions. Evidence as to the position of the double bonds in diethoxyhexadiene was obtained by

ozonisation : the ozonide yielded with water γ-ethoxycrotonaldehyde, ethoxyacetaldehyde, and the corresponding acids.

$$EtO\cdot CH_2\cdot CH{:}CH\cdot CH{:}CH\cdot CH_2\cdot OEt \longrightarrow \begin{matrix} EtO\cdot CH_2\cdot CH{:}CH\cdot CHO \\ \downarrow \\ EtO\cdot CH_2\cdot CH{:}CH\cdot CO_2H \end{matrix} + \begin{matrix} EtO\cdot CH_2\cdot CHO \\ \downarrow \\ EtO\cdot CH_2\cdot CO_2H \end{matrix}$$

The constitution of the parent dibromide follows from that of its diethoxy-derivative. It is true that change of substituent position during the transformation with sodium ethoxide is not entirely out of the question, but this possibility is discounted by several considerations. Not only was there no positive indication of such change, but degradation of the ozonide of the dibromide repeatedly failed to yield any recognisable trace of formaldehyde or of formic acid; the high boiling point of the dibromide compared with those of its isomerides was also in keeping with the 1 : 6-constitution. Thus a 3 : 4-glycol yields a 1 : 6-dibromide and the hydrocarbon derived from the latter adds bromine terminally.

Evidence bearing on the change from 3 : 4-glycol to 1 : 6-dibromide was furnished by the parent dibromide of the new hexatriene. This lost hydrogen bromide with such facility that the corresponding diacetate, diethoxy-compound, and glycol were unobtainable from it : it yielded a hydrocarbon, C_6H_6, of strong acetylenic odour and a bromohexatriene—a mode of reaction pointing to the constitution (VI).

$$\underset{\text{(VI.)}}{CH_2{:}CH\cdot CHBr\cdot CHBr\cdot CH{:}CH_2} \xrightarrow[NaOH]{\text{alc.}} \begin{cases} CH_2{:}CH\cdot CH{:}CBr\cdot CH{:}CH_2 \\ CH_2{:}CH\cdot C{:}C\cdot CH{:}CH_2 \end{cases}$$

This constitution is, moreover, the only one which permits of debromination without necessitating general valency rearrangement. As such rearrangement would lead in all probability to a *trans*-form, the new hydrocarbon, which has the slightly lower boiling point, is regarded as a *cis*-form.

Whether or no the 3 : 4-dibromide (A) consists essentially of one stereoisomeric form is uncertain. The preferential disappearance

$$\begin{array}{lccc} & CH_2{:}CH\cdot \underset{OH}{CH}\cdot CHBr\cdot CH{:}CH_2 & \longrightarrow & CH_2{:}CH\cdot \underset{OH}{CH}\cdot CH{:}CH\cdot CH_2Br \\ (a) & \uparrow & & \downarrow \\ & \text{Glycol} & & 1:6\text{-dibromide} \\ & \downarrow & & \uparrow \\ (b) & 3:4\text{-dibromide} & \longrightarrow & 1:4\text{-dibromide} \end{array}$$

of one stereoisomeric configuration in the change 3 : 4-glycol ⟶ 3 : 4-dibromide ⟶ 1 : 6-dibromide is conceivable, but there are

indications that to some extent the change proceeds as in scheme (*a*). Of the alternative scheme (*b*), which involves complete bromination before isomerisation, it may be said that efforts directed towards detecting the presence of the intermediate 1 : 4-dibromide gave no positive result. The yield of hydrocarbon repeatedly obtained from (A) (30%) was consistent with the presence of a proportion of less readily debrominated dibromide but was equal to that of van Romburgh's hydrocarbon from the homogeneous form (B).

Migration of Bromine.

The formation of the 1 : 6-dibromide from the 3 : 4-glycol has every appearance of involving the migration of bromine. If of common occurrence, the existence of such a facility is a consideration of the utmost importance in arriving at a *generalised* representation of the reactive form of conjugated hydrocarbons. The phenomenon is already known in the saturated hydrocarbon series (Lucas and Jameson, *J. Amer. Chem. Soc.*, 1924, **46**, 2476) and there is accumulating a considerable body of evidence that bromine migration in unsaturated hydrocarbons happens frequently; further, the general tendency of such halogen movement appears to be towards the assumption of terminal position with respect to a previously conjugated unit. Illuminating instances are those of hydrogen bromide addition to isoprene and $\beta\gamma$-dimethylbutadiene (Claisen, *J. pr. Chem.*, 1922, **105**, 68; Bergmann, *J. Russ. Phys. Chem. Soc.*, 1920, **52**, 37). In both cases, the first-formed tertiary bromide arising by 1 : 2-addition isomerises to a primary bromide, apparently the result of terminal addition; both changes are unexplainable by hydrogen migration. The question as to the primary or secondary nature of an additive product is vital, and if facile change from a primary to a secondary product is prevalent where bromine is the addendum, it is also to be suspected, speaking of hydrocarbons, where hydrogen is the addendum; in the latter case, however, proof is exceedingly difficult for obvious reasons.

The number of well-authenticated instances of 1 : 4-addition to hydrocarbons is very small. The production of a 1 : 4-dibromide from isoprene has recently been established (Bergmann, *loc. cit.*, p. 24; Staudinger, *Helv. Chim. Acta*, 1922, **5**, 756); the formation of a considerable proportion of the 1 : 2-dibromide of butadiene along with the 1 : 4-product is recorded by Straus as a private communication from Thiele (*Ber.*, 1909, **42**, 2872), and the formation of a 1 : 4-dibromide of *cyclo*pentadiene is recorded by Thiele (*Annalen*, 1900, **314**, 296). The behaviour of butadiene, isoprene, and *cyclo*pentadiene is at present being further examined, but in 1909 Straus (*loc. cit.*) expressed the opinion that whilst 1 : 4-addition

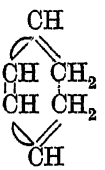
may occur, it is not the rule. He went beyond this in stating that no case was then known, at least among open-chain compounds, where 1 : 4-addition took place exclusively. Straus's further reflexion concerning the gloomy prospect afforded by the necessity of exhaustively determining the constitution of each single additive product before judging the position of entering halogen atoms suggests either a specific additive mode for each substance, or rather (since the reactive form of the addendum, molecular or atomic, is regarded as a possible contributing feature) that the joint relation of unsaturated hydrocarbon and addendum is specific. Leaving out of consideration the reactive form of the addendum, the formation of two or more additive dibromides for any conjugated hydrocarbon may be viewed in two ways: either the latter has two or more distinct tendencies towards reaction, possibly expressible by an equilibrium between reactive forms (compare Chandrasena and Ingold, J., 1922, **121**, 1312), or one or more of the products arise by secondary process—in the latter case the isomeric change is in no wise dependent on the reactive form of the parent hydrocarbon. For an equilibrium between the reactive forms of hydrocarbons there is no direct experimental evidence (compare Farmer and Healey, this vol., p. 1060).

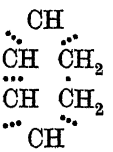
Yet van Romburgh's hexatriene adds bromine terminally. Obviously, if the foregoing considerations hold good, the 1 : 6-product may be no less a secondary product than the same compound is when formed from a 3 : 4-glycol. Since free hydrogen bromide and possibly free bromine are promoters of migratory changes, the use of a brominating agent other than commercial bromine is indicated in striving to isolate the primary additive bromide. Gupta and Thorpe (J., 1922, **121**, 1896) have investigated the employment of dibromodimethyldihydroresorcinol as a source of bromine in substitution reactions, and Rosenmund and Kuhnhenn (*Ber.*, 1923, **56**, 1262) have used the hydrobromide of quinoline dibromide with success in both substitution and additive reactions. When the quinoline derivative is employed with van Romburgh's hexatriene, instead of complete transformation into the solid dibromide, the latter (B) is replaced to a large extent (usually about 65%) by a new liquid dibromide (D), which is comparatively stable at room temperature but is converted (with slight decomposition and evolution of a little hydrogen bromide) into the

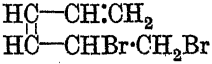
(VII.) $CH_2{:}CH{\cdot}CH$
 $\quad\quad\quad

with alcoholic alkali. With this reagent, as anticipated, (D) did not yield an acetylenic hydrocarbon, nor did it yield a diethoxy-derivative—a circumstance rendering a *cis-cis-* or *cis-trans*-1 : 6-configuration highly improbable—but conversion into a bromohexatriene readily took place. The further characterisation of the dibromide (VII) and its derivative (probably VIII) was not possible with the material at disposal.

Turning to *cis*-hexatriene, residual valency or electronic formulæ such as (IX) and (X) automatically disappear with the denial of an activated form in which the three unsaturated centres of the chain are fused.

(IX.) 

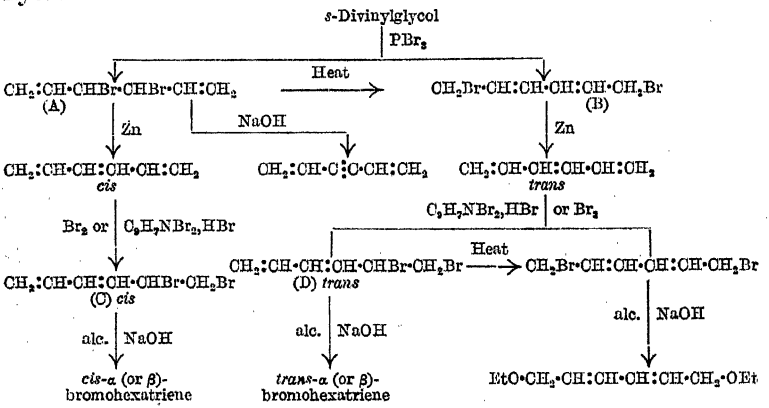
(X.) 

 (XI.)

But whether the reactive form of the hydrocarbon is an open-chain or pseudo-cyclic structure, the formation of a 1 : 6-dibromide would be expected to result in the appearance of the solid (B), since the necessary valency adjustment consequent on addition should lead to the assumption of the *trans-trans*-configuration no less than in the case of addition to *trans*-hexatriene. Both hexatrienes being regarded as open-chain forms, then of those additive modes which would tend to destroy differentiation between the respective additive products there are 1 : 6 (compelling valency reorganisation), 3 : 4 (removing the double bond which is the seat of geometrical isomerism) and 1 : 4 (compelling valency reorganisation). Neglecting 1 : 3-, 3 : 5-, etc., forms, there is left only the 1 : 2-form, so that the only distinction between the 1 : 2- dibromides from the two hydrocarbons should be one of spatial distribution as in (VII) and (XI).

It was found by experiment that the dibromide (C) from the new hexatriene behaved in quite different fashion from the known 1 : 6- and 3 : 4-forms. It was not convertible into an acetylenic hydrocarbon or a diethoxy-derivative, but, like the labile product (D) from van Romburgh's hexatriene, readily yielded with alkali a bromohexatriene. The great difference between the forms (C) and (D) is the tendency towards bromine migration in the latter contrasting with the high degree of stability of the former. This difference is quite compatible with the different steric conditions in the two compounds and it is probably that the dibromide (C) obtained by using commercial [illegible] appeared in every

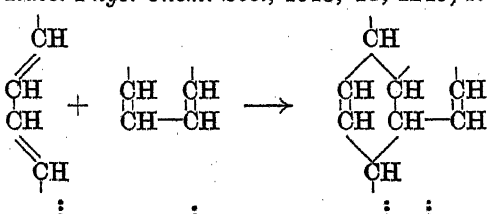
respect identical with that obtained by using quinoline dibromide hydrobromide.



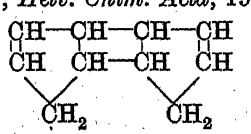
The halogen atoms of certain of the additive dibromides of this series possess marked lability : *e.g.*, the dibromide of 1 : 6-diphenylhexatriene reverts to the hydrocarbon on treatment with diethylamine or pyridine, whilst the dibromides (A) and (B) readily liberate iodine from potassium iodide acidified with acetic acid. This lability, which has not as yet been extensively examined, varies considerably with the nature, and possibly the spatial distribution, of the groups R, R′ in the complex R·CHBr·R′. For instance, whilst diphenylhexatriene dibromide loses its bromine with pyridine as noted above, the solid hexatriene dibromide (B) yields a stable pyridinium salt of type PyBr–CH_2·CH:CH·CH:CH·CH_2–PyBr and analogous compounds with diethylamine and aniline. Evidence on the subject of bromine migration is furnished by Prévost in two papers which escaped the authors' notice until a late stage in the investigation. It is shown (*Compt. rend.*, 1926, **183**, 1292) that erythrol, CH_2:CH·CH(OH)·CH_2·OH, when treated with phosphorus tribromide in pyridine solution, yields not the expected 1 : 2-dibromo-Δ^3-butene, but 1 : 4-dibromo-Δ^2-butene, CH_2Br·CH:CH·CH_2Br. Thus the transformation already known to take place when the hydroxyl groups of substituted vinylcarbinols are replaced by bromine, R·CH(OH)·CH:CH_2 $\xrightarrow{PBr_3}$ R·CH:CH·CH_2Br, is repeated with vinylglycol (erythrol). Consequently the suspicion arose that *s*-divinylglycol might behave similarly, and this author enumerates (*Compt. rend.*, 1927, **184**, 458) certain observations of Griner (*loc. cit.*) that are inconsistent with a 3 : 4-constitution for solid hexatriene dibromide. In support of this view, he succeeded in obtaining from the latter glycol and the corresponding diacetate which differed in properties from *s*-divinylglycol and its diacetate;

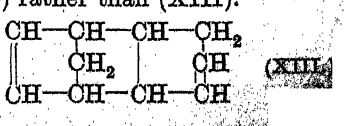
moreover, the molecular exaltations of these two derivatives are consistent with the constitutions $HO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$ and $AcO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OAc$ respectively.

The chemistry of hexatriene is intelligible on the basis of bromine migration in a non-conjugated system, but although it is clear that a terminal additive product is by no means the necessary outcome of primary additive reaction, and although it may be demonstrable that a terminal product may arise merely by isomerisation of a different additive form, there is as yet no certainty that it may not also arise as a primary product of addition. Thus whilst there can be no other conclusion than that the attempts which have been made from time to time (compare Allsop and Kenner, J., 1923, **123**, 2296) to retain the Thiele hypothesis by restricting its scope to conjugated hydrocarbons cannot stand when bromine and hydrogen bromide are the addenda considered, it is possible that the modern extension of the Thiele hypothesis which allows of two or more types of polarisation, one or more of which may come into play as determined by the nature and reactive condition of the addendum, may cover the experimental observations. At the same time, the extent to which addition to an unsaturated compound may be considered as determined by unsaturated compound and addendum separately is by no means clear. In this respect polymerisation processes are of great interest. If butadienoid compounds in general polymerise in the manner suggested by Lebedef (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249) it would seem



that the forms $\cdot CH{:}CH{\cdot}CH{:}\dot{C}H$ and $CH{:}CH{\cdot}\dot{C}H{:}\dot{C}H$ (or their electronic equivalents) may co-exist and that additive mode is determined by the reactive state of each particular addendum. The usual co-existence of such forms would account for the difference between the recorded tendencies towards polymerisation of open-chain butadienes and *cyclo*pentadiene, the latter yielding under the exigencies of spatial configuration a dimeride (XII) (Staudinger, *Helv. Chim. Acta*, 1924, **7**, 23) rather than (XIII).

(XII.) 



Nevertheless the appearance of ready isomerisation among the products of addition to conjugated hydrocarbons is a factor demanding consideration in estimating the significance of current reaction formulæ. It is hoped shortly to submit further evidence on the subject of *primary* additive products.

EXPERIMENTAL.

s-*Divinylglycol.*

Reduction.—The glycol (prepared in large quantities from the pure stabilised acraldehyde of Messrs. Poulenc Frères by the method of Griner, *loc. cit.*) was reduced at atmospheric pressure and room temperature with palladium and hydrogen. Absorption was rapid and somewhat exceeded the requirements of simple hydrogenation —a fact explained by the formation of some quantity of a volatile alcohol, presumably ethylpropylcarbinol. On working up the product in the usual way, a liquid was obtained; one portion of this (b. p. 87—89°/15 mm.) remained almost completely liquid at —20°, whilst the remainder (b. p. 89—91°/15 mm.) solidified in the receiver of the apparatus. The former, after being freed as far as possible from the latter and redistilled, was obtained as a colourless, mobile oil, b. p. 87—88°/15 mm. (Found: C, 60·6; H, 11·8. $C_6H_{14}O_2$ requires C, 61·0; H, 11·9%). The latter crystallised from light petroleum in white plates, m. p. 88° (Found: C, 60·5; H, 11·8%). Both substances gave good yields of propionic acid (identified as the anilide, m. p. 105°) when carefully oxidised with dilute potassium permanganate. They must therefore be stereoisomeric forms of s-*diethylethylene glycol.*

Bromination.—Numerous methods of halogenation were tested. The most satisfactory reagent was phosphorus tribromide. Griner's procedure (*loc. cit.*, p. 380) was followed, but it was found advantageous to employ a mechanical stirrer and extract the product (after pouring on ice) with ether. The well-washed extract was dried and the main bulk of solvent removed on a steam-bath. The remaining ether was removed at reduced pressure, and the residual oil diluted with light petroleum and cooled in a freezing mixture. The crystals of dibromide (B) (m. p. 85°) which separated were removed and the procedure of cooling and filtering twice was repeated. The ultimate filtrate was freed from solvent as above, and the residual oil fractionated. To avoid gross decomposition, it was necessary to distil the crude liquid, first, at 1 mm. pressure; subsequently three fractions were collected, (*a*) a small portion boiling below 80°/11 mm., (*b*) b. p. 80—115°/11 mm., (*c*) b. p. 115—140°/11 mm. The portion (*b*), on redistillation, passed over

almost entirely at 80—95°/10 mm.; this material corresponded in composition approximately with hexatriene dibromide, but contained a material which caused considerable carbonisation on standing for a few hours. To obtain some idea of the correct boiling point of the pure dibromide, the sub-fractions indicated were analysed ($C_6H_8Br_2$ requires C, 30·0; H, 3·4; Br, 66·6%).

	Percentage composition.		
B. p.	C.	H.	Br.
80—87°/10 mm.	32·2	4·4	63·4
88—92°/11 mm.	31·0	4·1	—
90—95°/10 mm.	31·1	3·9	65·0
90—96°/11 mm.	30·0	4·0	64·7

Finally, a considerable quantity of a pale yellow oil (A), b. p. 94—96°/11 mm., was obtained, which was used in subsequent operations (Found: C, 30·0; H, 3·6; Br, 66·6%). This substance could not be kept for many days at room temperature owing to the rapidity of carbonisation.

The higher-boiling material, after separation by the above-described method of a quantity of solid dibromide which commenced to crystallise on cooling, consisted mainly of a yellow oil, b. p. 135—140°/11 mm. This was evidently a *tribromohexene* (Found: Br, 73·1. $C_6H_9Br_3$ requires Br, 74·8%). It was subsequently found that the proportion of this substance was greatly reduced when bromination was effected by gradually pouring a chloroform solution of the glycol into a chloroform solution of phosphorus tribromide. With this procedure, however, it was particularly necessary to avoid undue heating of the crude mixture of bromides whilst removing the solvent.

Dibromide (A) *and its Derivatives.*

γδ-Dibromo-$\Delta^{\alpha\epsilon}$*-hexadiene.*—All attempts to demonstrate the constitution of the dibromide (A) by direct oxidation failed. The assigned formula rests upon the properties of the substance in relation to those of the three isomeric dibromides.

(a) *Isomeric Change.*—It was repeatedly observed during distillation of this liquid that a portion of the material suffered change of boiling point. This was not very marked at pressures of 1—4 mm., degradation (accompanied by liberation of hydrogen bromide) then being slight, but was much more marked at pressures of 10—22 mm., degradation being appreciable. From the higher-boiling portions so produced, crystals of the solid dibromide invariably separated. The loss of material sustained in this way was considerable and in conjunction with the initial low yield of crude bromides rendered

the accumulation of adequate quantities of reasonably pure liquid dibromide very laborious.

(b) *Ease of Hydrogen Bromide Removal.*—Numerous attempts were made to prepare the glycol and the diacetate of the glycol corresponding to this dibromide. In every case, owing to the loss of hydrogen bromide, the product was a mixture of substances of very different boiling point from which no pure substance could be fractionated. With alcoholic sodium ethoxide, loss of hydrogen bromide was still more complete: a $\gamma\delta$-diethoxyhexadiene was therefore unobtainable.

For rapid removal of hydrogen bromide alcoholic sodium hydroxide was found to be the best reagent. Sodium ($1\frac{1}{2}$ atoms) was dissolved in aqueous alcohol, and the cold solution added gradually, with shaking, to an alcoholic solution of the dibromide (1 mol.). The separation of sodium bromide was completed by heating the mixture for a few minutes on a steam-bath, after which the product was cooled and poured into water. An oil was precipitated: this was well washed with water, dried with calcium chloride, and fractionated. Two fractions were collected, (*a*) b. p. 80—95° and (*b*) b. p. 50—60°/22 mm. Redistillation of the former yielded a colourless, mobile hydrocarbon of penetrating, acetylenic odour. The ease with which this substance, doubtless $\Delta^{\alpha\epsilon}$-*hexadien-γ-in*, polymerised rendered purification and analysis very difficult, and a detailed study of its properties impossible (Found: C, 91·1; H, 7·2. C_6H_6 requires C, 92·3; H, 7·7%). The fraction (*b*) yielded a faintly yellow liquid, b. p. 52—55°/20 mm., which could not be completely freed from the polymeric products of the hydrocarbon. This substance, which polymerised completely in 24 hours, resembled, in its very characteristic odour, the bromohexatrienes later described. There can be little doubt that it was *γ-bromohexatriene* (Found: Br, 49·3. C_6H_7Br requires Br, 50·3%).

(c) *Bromine Addition.*—The dibromide, dissolved in chloroform, absorbed bromine readily at first, but later absorption was slow. After removal of the solvent at reduced pressure and distillation, the tetrabromide (presumably $\alpha\beta\gamma\delta$-*tetrabromo*-Δ^{ϵ}-*hexene*) was obtained as a yellow oil (b. p. 155—158°/11 mm.) which remained liquid at −25° (Found: Br, 79·7. $C_6H_8Br_4$ requires Br, 80·0%).

cis-Hexatriene.—To 3 : 4-dibromohexadiene, dissolved in 5 times its bulk of 98% alcohol, excess of zinc dust was added in small amounts, the reaction mixture being finally heated for 20 minutes on a steam-bath. The zinc residue was filtered off and the filtrate poured into several times its bulk of water. The oily layer was separated and washed ten times with small quantities of water. Subsequent drying over calcium chloride and distillation yielded a

colourless liquid (b. p. 75—83°) and a considerable quantity of high-boiling material. On redistillation the former boiled at 78·5°/760 mm. Yield 30%. This hydrocarbon resembled van Romburgh's hexatriene in odour and in proneness to polymerisation; the latter property in conjunction with high volatility rendered analysis difficult. The density and molecular exaltation ($d_4^{20°}$ 0·7175; $n_D^{20°}$ 1·4577; $[R_L]_D$ 30·41) are lower than the latest values recorded by van Romburgh for the isomeric hydrocarbon (Found: C, 88·5; H, 11·6. C_6H_8 requires C, 90·0; H, 10·0%). It is probable that the new hydrocarbon contained van Romburgh's hexatriene to the extent of 2—2½%.

Dibromide (C) *and its Derivatives.*

cis-αβ-*Dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene.*—Bromine (2 atoms) was added to a chloroform solution of *cis*-hexatriene kept below 0°. Addition was very rapid. The product, after removal of the solvent at reduced pressure, was a colourless oil (all the other dibromides were yellow in liquid form), b. p. 90—96°/11 mm. (Found: Br, 66·5. $C_6H_8Br_2$ requires Br, 66·6%). There was a very small residue of the solid dibromide (B), representing about 1½—2½% of the hexatriene employed.

A colourless, stable dibromide quite indistinguishable from the above was obtained by employing quinoline dibromide hydrobromide in place of free bromine (method of Rosenmund and Kuhnhenn, *loc. cit.*). The acetic acid solution of the product was poured into ice-water, and the oily dibromide extracted with ether. It was necessary to remove the usual small amount of solid dibromide (B) before distillation.

The corresponding tetrabromide (tetrabromohexene) was obtained by employing 4 atoms of bromine instead of 2 atoms. It consisted of a large proportion of a yellow oil, b. p. 155—158°/11 mm. (Found: Br, 79·8. $C_6H_8Br_4$ requires Br, 80·0%), and a very small proportion of a solid which crystallised from petroleum in colourless needles, m. p. 91° (Found: C, 18·1; H, 2·7; Br, 79·6. $C_6H_8Br_4$ requires C, 18·0; H, 2·0; Br, 80·0%).

cis-α(or β)-*Bromohexatriene.*—The dibromide (C) (1 mol.) was dissolved in a little alcohol and to it an alcoholic solution of sodium ethoxide (2 mols.) was added drop by drop with shaking. The reaction was completed by heating the mixture for ½ hour on a steam-bath. On cooling and pouring the mixture into water an oil was precipitated. This was extracted with ether and dried, and the solvent removed under a column. The residue, which contained no volatile hydrocarbon, was distilled. An almost colourless liquid possessing the characteristic bromohexatriene odour pass-

over at 45—65°/20 mm., leaving much material, apparently the product of extensive polymerisation. On redistillation, the bulk of the distillate boiled at 52—55°/20 mm. (Found : Br, 48·5. C_6H_7Br requires Br, 50·3%). This substance polymerised extensively in 24 hours.

Dibromide (B) *and its Derivatives.*

αζ-Dibromo-Δ$^{\beta\delta}$-hexadiene.—Numerous attempts were made to demonstrate the constitution of Griner's solid dibromide (m. p. 85°) directly. As these had little success, the constitution of its diethoxy-derivative (below) was fully examined, the possibility of isomerisation during conversion being discounted by many observations.

The two forms of the corresponding tetrabromide (possibly *αβεζ-tetrabromo-Δ$^{\gamma}$-hexene*) are incorrectly described by Griner (*loc. cit.*, p. 383). The less soluble isomeride, after successively crystallising from chloroform and light petroleum, yielded colourless prisms, m. p. 111° (Found : Br, 80·0. Calc. : Br, 80·0%); the more soluble separated from light petroleum in colourless prisms, m. p. 46° (Found : Br, 80·3%). These tetrabromides showed very great stability towards oxidation by ozone and by permanganate.

Behaviour with Organic Bases.—When a dry ethereal solution of pyridine (2 mols.) was added to a dry solution of the solid dibromide (B) a bulky precipitate separated. This substance, which was readily soluble in water, appeared to be quite free from pyridine hydrobromide. It crystallised from alcohol–ether in colourless plates, m. p. 212°, and appeared to be the *dipyridinium* salt, PyBr–CH_2·CH:CH·CH:CH·CH_2–PyBr (Found : Br, 41·2. $C_{16}H_{18}N_2Br_2$ requires Br, 40·2%). Analogous compounds were formed with aniline and diethylamine, but were not further investigated. Dry distillation of the dipyridinium compound yielded a large amount of pyridine dibromide and a minute quantity of a liquid with a garlic-like odour.

αζ-Diacetoxy-Δ$^{\beta\delta}$-hexadiene.—A mixture of the dibromide (50 g.) with glacial acetic acid (50 g.) was added to excess of potassium acetate moistened with glacial acetic acid (50 g.). The whole was heated on a steam-bath for 24 hours. The cooled mass was poured into water, and the product isolated in the usual way. As it still contained bromine, it was heated for a further period with potassium acetate and acetic acid. Finally a product almost free from bromine was obtained. The bulk of this distilled at 155—160°/14 mm. as a colourless oil (Found : C, 60·8; H, 7·0. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%).

αζ-Diethoxy-Δ$^{\beta\delta}$-hexadiene.—The solid dibromide (B) was added to the requisite quantity of thoroughly cooled alcoholic sodium

ethoxide. The product was well shaken and gradually heated till ebullition set in. The reaction was completed by heating for ¾ hour on a steam-bath. After cooling, the reaction mixture was poured into water, and the precipitated oil extracted with ether. The diethoxy-compound was obtained in almost quantitative yield as a colourless, mobile oil (b. p. 116°/20 mm.) of characteristic odour (Found: C, 70·5; H, 10·8. Calc.: C, 70·6; H, 10·6%). This corresponds to Griner's product (regarded as γδ-diethoxy-$\Delta^{\alpha\epsilon}$-hexadiene) obtained by the action of alcoholic potash on the same dibromide (*loc. cit.*, p. 388).

Reduction of αζ-Diethoxy-$\Delta^{\beta\delta}$*-hexadiene.*—Diethoxyhexadiene (10 g.) was reduced with colloidal palladium and hydrogen at room temperature and atmospheric pressure. Reduction was rather slow at the beginning but became rapid later and was complete in about 3½ hours. The amount of hydrogen absorbed was about 35% in excess of that theoretically required for reducing two double bonds. On pouring the reaction mixture into water and working up in the usual way the product was found to consist of two substances, (*a*) a colourless liquid of strong odour (b. p. 38—45°/14 mm.), appreciably volatile in ether vapour and very volatile in alcohol vapour, and (*b*) a less volatile, colourless liquid (b. p. 80—90°/14 mm.). The former (about 5 g.), which was almost certainly *α-ethoxyhexane*, distilled completely at 42°/14 mm., but was not quite free from the second product (Found: C, 72·2; H, 13·0. $C_8H_{18}O$ requires C, 73·8; H, 13·8%); the latter (about 3 g.), which possessed a faint odour and distilled at 86°/14 mm., was *αζ-diethoxyhexane* (Found: C, 70·2; H, 12·5. $C_{10}H_{22}O_2$ requires C, 70·0; H, 12·6%).

αζ-Di-iodohexane.—Diethoxyhexane contained in a Carius tube was saturated with dry hydrogen iodide, the weight of gas absorbed being noted. The tube was sealed and heated at 100° for 16 hours. It was then cooled, opened, and re-treated with hydrogen iodide until the requisite quantity of this gas (2 mols.) had been absorbed. It was again heated for 16 hours. The cooled product consisted of a small, colourless layer which seemed to be mainly alcohol (free from any considerable amount of ethyl iodide) and a heavy, dark brown layer. The latter was dissolved in ether, washed with sodium bicarbonate solution and water, and dried with calcium chloride. This crude di-iodohexane, which was only slightly deficient in iodine, was converted into the corresponding dinitrile without further purification.

αζ-Dicyanohexane.—The crude di-iodohexane was converted into the dinitrile with potassium cyanide as described by Hamonet (*Compt. rend.*, 1903, **136**, 244). The dinitrile was isolated by pouring the reaction product into water and extraction with ether. The

dried extract gave a good yield of a pale yellow oil, which differed from the di-iodide in its ready solubility in alcohol.

Suberic acid. When heated with concentrated hydrochloric acid for 1 hour, the crude dinitrile was hydrolysed and gave an excellent yield of suberic acid, which separated from water in colourless needles, m. p. 138°, mixed m. p. 138° [Found : C, 55·2; H, 7·9; *M* (dibasic), 177. Calc. : C, 55·2; H, 8·0%; *M*, 174].

Oxidation of αζ-Diethoxy-$\Delta^{\beta\delta}$*-hexadiene.*—A stream of ozonised oxygen was passed for 14 hours through a chloroform solution of this substance. The solvent was then removed at reduced pressure. The colourless, syrupy ozonide was shaken with 50 c.c. of water, and the mixture warmed until complete decomposition took place (85°). The yellow aldehydic oil was separated from the aqueous layer and dissolved in ether. From the ethereal extract, freed from acidic matter by shaking it several times with dilute bicarbonate solution, and dried with calcium chloride, the aldehyde was obtained as a mobile, pungent-smelling oil; from the alkaline washings a yellow syrupy acid was extracted by ether. This gave an aldehydic reaction, but deposited, on long standing in a vacuum desiccator, a few crystals (long, colourless prisms, m. p. 45°) of a non-aldehydic acid. The combination of melting point, equivalent (micro-titration, 135), unsaturated nature, and its ready solubility in water and petroleum suggested that the latter acid was γ-ethoxycrotonic acid (compare Lespieau, *Compt. rend.*, 1905, **140**, 723). This was subsequently confirmed (below).

The residual syrupy acid was fractionated. The bulk distilled at 106—107°/21 mm. as a colourless, mobile liquid. Since the basicity of this substance was nearly that of ethoxyacetic acid (the degradation product complementary to γ-ethoxycrotonaldehyde), it was converted into the *p*-bromophenacyl ester. An excellent yield of *p*-bromophenacyl ethoxyacetate was obtained therefrom by the method of Judefind and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1047) : this crystallised in colourless plates, m. p. 104·5°, and agreed in properties with the product described by these authors (Found : C, 48·1; H, 4·4. Calc. : C, 47·8; H, 4·3%).

The aldehydic oil was separated into four fractions by distillation, (*a*) below 75°/21 mm., (*b*) 75—85°/21 mm., (*c*) 85—100°/21 mm., and (*d*) a viscous residue which partly distilled on strong heating to yield a colourless, mobile oil which polymerised to a jelly on standing for several days. Of these fractions, (*b*) and (*c*) constituted the bulk of material. The former, which distilled almost completely at 80°/21 mm., did not yield a semicarbazone or phenylhydrazone but corresponded in composition with *γ-ethoxycrotonaldehyde* (Found : C, 62·8; H, 8·9. $C_6H_{10}O_2$ requires C, 63·1; H, 8·8%). This

constitution was confirmed by oxidation (below). From fraction (*a*) a small quantity of impure ethoxyacetaldehyde (b. p. 70°) was isolated. As this was insufficient for adequate fractionation, it was oxidised to ethoxyacetic acid (below).

Oxidation of γ-Ethoxycrotonaldehyde and Ethoxyacetaldehyde.—These oxidations were conducted in almost exactly the way described by Delépine and Bonnet (*Compt. rend.*, 1909, **149**, 39). The former yielded a solid acid which crystallised from light petroleum in colourless prisms, m. p. 45°. This acid was γ-ethoxycrotonic acid [Found: C, 55·2; H, 7·6; *M* (monobasic), 133. Calc.: C, 55·4; H, 7·7%; *M*, 130] and was identical with that formed directly during the decomposition of the ozonide.

The oxidation product of ethoxyacetaldehyde was a liquid. This was identified as ethoxyacetic acid by conversion into the *p*-bromophenacyl ester described above.

trans-*Hexatriene.*—Van Romburgh's hydrocarbon, regarded as *trans*-hexatriene, was prepared from the dibromide (B) as described for the *cis*-compound.

As observed by van Romburgh, when a chloroform solution of bromine (1 mol.) was added to a chloroform solution of the hydrocarbon (1 mol.) at 0°, conversion into the solid dibromide (αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene) was complete.

Dibromide (D) *and its Derivatives.*

trans-αβ-*Dibromo*-$\Delta^{\nu\epsilon}$-*hexadiene.*—When quinoline dibromide hydrobromide (1 mol.) was gradually added at 0° to a well-agitated solution of the *trans*-hydrocarbon in glacial acetic acid, bromination was readily effected. The product was poured into ice-water, and the oily suspension filtered. After removal of a quantity of the solid bromide (B) by filtration the filtrate was extracted with ether. The extract was washed until free from acetic acid and dried, and the ether was evaporated, finally under reduced pressure. The oily residue was dissolved in light petroleum and cooled to −25°; the solid dibromide which separated was filtered off and the cooling and filtering repeated. After removal of the bulk of the solvent by gentle heating and of the remainder under reduced pressure, a yellow oil was obtained (yield, 65%) (Found: Br, 65·2. $C_6H_8Br_2$ requires Br, 66·6%). A small quantity of this distilled under 1—2 mm. pressure without apparent decomposition. When cautious distillation of a larger portion at 22 mm. pressure was attempted, the distillation of the first few drops (b. p. 107°/21 mm.) was concurrent with a rapid darkening in colour and a slight evolution of hydrogen bromide. Isomeric change had taken place, for further distillation occurred only at a much higher temperature.

On cooling, the contents of the flask, which had previously remained liquid at — 25°, set to a solid mass of the dibromide (B). The extent of conversion of the liquid to the solid dibromide was very high.

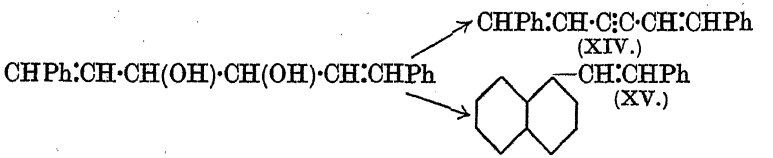
trans-α(or β)-*Bromohexatriene.*—Removal of hydrogen bromide from the liquid *trans*-αβ-dibromohexadiene (above) was effected precisely as with the corresponding *cis*-compound (p. 2949). Much polymerisation appeared to have occurred during the reaction, for only a portion of the product was distillable. A faintly yellow liquid, b. p. 53°/22 mm., was obtained which possessed the characteristic odour of bromohexatriene (Found: Br, 48·2. C_6H_7Br requires Br, 50·3%). This substance polymerised the most rapidly of the three isomerides: within 15 minutes of distillation a scaly deposit appeared on the sides of the vessel and within 2 hours the change was complete.

Derivatives of αζ-Diphenylhexatriene.

s-*Distyrylethylene Glycol* (*Hydrocinnamoin*).—Reduction of cinnamaldehyde was effected by Thiele's method (*Ber.*, 1899, **32**, 1296). Separation of the solid glycol from the viscous oil was best effected by completely dissolving the latter in hot alcohol and cooling the solution in a freezing mixture. The crystals so obtained, when washed with a little ether and recrystallised once from alcohol, attained at once the correct melting point (153—154°). Yield 10—12%.

The residual viscous oil was treated with steam to remove volatile matter, cooled, dissolved in ether and dried over sodium sulphate. Removal of the solvent left a transparent jelly, which was kept in an evacuated desiccator for a week. Portions of the substance were examined in the following manner to ascertain whether it contained isomeric distyrylglycols or their corresponding hydrocarbons: (a) *Distillation.* About half the material distilled between 110° and 200° at 3 mm.; the remainder was undistillable (solid distyrylethylene glycol distils readily at 2 mm.). The portion, b. p. 130—200°/3 mm., deposited colourless plates, m. p. 206°, which dissolved in ether and benzene to give fluorescent (bluish) solutions. This hydrocarbon had previously been noted by Thiele (*loc. cit.*), and his view that it may be phenyl-α-naphthylethylene appears to be correct: the substance is unimolecular in benzene solution, and of the dehydration products (XIV) and (XV) the latter accounts for our inability to effect any reduction with hydrogen and colloidal palladium (Found: C, 93·9; H, 5·5; *M*, cryoscopic, 225. Calc.: C, 93·9; H, 6·0%; *M*, 230). (b) *Dehydration.* When the material was heated with acetic anhydride for 4 hours at 150°, two substances were obtained, the hydrocarbon (XV) and an oil (more mobile than

the original one) from which no definite product could be isolated. (c) *Attempted benzoylation.* Treatment with benzoyl chloride



(Schotten–Baumann conditions) yielded again the hydrocarbon (XV). (d) *Bromination.* Addition of bromine yielded no identifiable product, but phosphorus tribromide gave a small quantity of the diphenyldibromohexadiene, m. p. 124°, described below, and other non-purifiable products.

Dibromo-αζ-diphenylhexadiene.—To phosphorus tribromide (20—25 g.), dissolved in dry ether at 0°, distyrylethylene glycol (5 g.) was added in small amounts, with vigorous shaking. The temperature was allowed to rise during addition and the product was kept at room temperature for ¾ hour. The mass was poured on ice and the pale yellow solid which was precipitated was filtered off and washed with ether. The filtrate was extracted with ether, and the extract thoroughly washed and dried. The bulk of the solvent was evaporated and the remainder removed under reduced pressure. The residue was a yellow, sticky mass which was freed from oil by washing with ether. The united solid portions were dried and recrystallised from petroleum, yielding colourless crystals (3·5 g.) of *dibromo-αζ-diphenylhexadiene*, m. p. 124—125° (Found: Br, 41·0. $C_{18}H_{16}Br_2$ requires Br, 40·8%). The ethereal washings yielded a small amount of a yellow oil, which was very unstable and rapidly caused the decomposition of the solid dibromide if left in contact with it. This substance was probably also a dibromide; mixtures of the two when treated with zinc yielded only the diphenylhexatriene described below.

αζ-Diphenylhexatriene.—To the dibromide, m. p. 124—125°, dissolved in 50 c.c. of chloroform, zinc dust (1 g.) was added in small portions with thorough shaking. The mixture was then warmed for ½ hour on a steam-bath. The cooled product, diluted with much ether, was washed with dilute sulphuric acid and water, and dried. On concentration and cooling, a crop of shining, yellow leaflets (m. p. 196°) separated. This hydrocarbon, which was crystallisable from chloroform, was undoubtedly the same diphenylhexatriene obtained by Smedley (J., 1908, 93, 376) through condensing sodium phenyl*iso*crotonate with cinnamaldehyde in presence of acetic anhydride (Found: C, 94·0; H, 6·6. Calc.: C, 93·7; H, 6·9%). Yield 60—65%.

Bromination of αζ-Diphenylhexatriene.—Addition of bromine (1 mol.) to the hydrocarbon (1 mol.) dissolved in a large bulk of carbon disulphide was effected at − 20°. When absorption, which was rather slow, was complete, the product was thoroughly washed and dried. Removal of the solvent yielded a solid which, after being washed with ether, was colourless and needed no further purification. This substance, m. p. 124—125°, was identical with the solid dibromide (dibromo-αζ-diphenylhexadiene) from which the hydrocarbon had been prepared. When thus obtained, it was quite free from the traces of impurities which promoted decomposition (Found : Br, 40·7%).

The *tetrabromide* and *hexabromide* were formed with increasing difficulty by further addition of bromine. The former crystallised in white prisms, m. p. 165° (Found : Br, 58·7. $C_{18}H_{16}Br_4$ requires Br, 57·9%), and the latter in stout needles, m. p. 228—230° (Found : Br, 67·8. $C_{18}H_{16}Br_6$ requires Br, 67·4%).

Action of Organic Bases on Diphenylhexatriene Dibromide.—Diethylamine (1 g.) was added to the dibromide (1 g.) dissolved in absolute ether. In 2 days a heavy precipitation (about 1 mol.) of pearly-white diethylamine hydrobromide, m. p. 212°, had taken place. This salt was removed and the ethereal solution was washed with dilute acid and with water and dried. On concentration, it deposited a considerable amount of pure diphenylhexatriene, m. p. 196°.

Pyridine also gave, under similar conditions, the same hydrocarbon.

Derivatives of αζ-Dimethylhexatriene [$\Delta^{\beta\delta}$-*Octatriene*].

s-*Dipropenylethylene Glycol.*—Crotonaldehyde was reduced in analogous manner to acraldehyde (compare Charon, *Ann. Chim. Phys.*, 1899, **17**, 266). The glycol, a faintly yellow oil, b. p. 120—122°/9 mm., was obtained in 50—60% yield.

Bromination of s-*Dipropenylethylene Glycol.*—The method which gave the best results is the following. The glycol (50 g.), dissolved in dry ether, was added drop by drop to a solution of phosphorus tribromide (200 g.) in dry ether (100 c.c.). At first the temperature was kept below 10°; later, occasional moderation by cooling kept it in the neighbourhood of room temperature. When addition was complete, the mixture was kept for ¾ hour and then poured on ice. After careful washing and drying, the major portion of the solvent was distilled from a steam-bath and the remainder at reduced pressure. No solid bromide was isolable and complete carbonisation of the crude liquid was avoided only by distillation at greatly reduced pressure, all access of air to the hot liquid being prevented.

At 1 mm. a large proportion distilled: this distillate yielded fractions 68—85°/14 mm., 85—100°/14 mm., and 100—120°/14 mm., all of which had nearly the correct bromine content. The substance obviously contained two or more isomeric dibromides along with small amounts of impurity which promoted rapid decomposition at room temperature. As adequate separation of the isomerides was impossible by fractionation, the above fractions were united and redistilled; a portion, b. p. 92—100°/14 mm., was utilised for subsequent experiments. This was an almost colourless liquid which darkened in a few hours and became almost black in 24 hours (Found: Br, 56·3. $C_8H_{12}Br_2$ requires Br, 59·7%).

αζ-Dimethylhexatriene.—The dibromide (30 g.) yielded with zinc and alcohol (see p. 2948) an oil, much of which distilled between 45° and 112° at 25 mm. Only the portion, b. p. 45—55°/25 mm., was bromine-free: this was redistilled at ordinary pressure and a fraction, b. p. 120—130°, was collected. Thus about 8 c.c. of a somewhat impure, colourless hydrocarbon of distinctive odour were obtained (Found: C, 84·8; H, 11·2. C_8H_{12} requires C, 89·9; H, 11·1%). This, on further fractionation through a small column, yielded 2 c.c. of hydrocarbon, b. p. 125—130° (Found: C, 87·7; H, 11·4%; $d_4^{18°}$ 0·8394; $n_D^{18°}$ 1·45193; $[R_L]_D$ 34·70). Numerous attempts to obtain purer and larger specimens of the hydrocarbon were made. The rapidity of polymeric and oxidative changes, however, caused great loss both during the debromination process and subsequently; soft, wax-like flakes rapidly appeared on the walls of the vessel containing the hydrocarbon and in a few hours the latter changed into a jelly.

βε-Dimethyl-αζ-diethylhexatriene [*δη-Dimethyl-Δ$^{\nu\epsilon\eta}$-decatriene*].

α-Methyl-β-ethylacraldehyde was prepared from propaldehyde by Döbner and Weissenborn's method (*Ber.*, 1902, **35**, 1144).

δη-Dimethyl-Δ$^{\nu\eta}$-decadiene-εζ-diol.—Methylethylacraldehyde was reduced in similar fashion to acraldehyde. The *glycol* was a rather viscous, yellow oil, b. p. 163—165°/23 mm. It was soluble in water and the common organic solvents and did not solidify at — 25° (Found: C, 72·8; H, 11·3; $d_4^{19°}$ 0·9400; $[R_L]_D$ 59·20. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·1%).

εζ-Dibromo-δη-dimethyl-Δ$^{\nu\eta}$-decadiene.—The glycol (20 g.) was added in drops to an ethereal solution of phosphorus tribromide (100 g.). After 1 hour, the mixture was poured on ice, and the dibromide extracted with ether. The dried ethereal solution yielded, on evaporation, a white, sticky mass: this was taken up in light petroleum and warmed with animal charcoal. After filtration, white

prisms, m. p. 99—100°, separated (Found: Br, 50·2. $C_{12}H_{20}Br_2$ requires Br, 49·4%).

βε-Dimethyl-αζ-diethylhexatriene.—By the action of zinc on dibromodimethyldecadiene (in alcoholic solution) a product of variable boiling point was obtained. Since even the lowest-boiling fraction still contained bromine, the whole was re-treated with zinc. Much polymeric change attended these operations, waxy scales separating on the sides of the containing vessel. A quantity of unsaturated hydrocarbon of strong odour (colourless liquid, b. p. 65—70°/26 mm.) was obtained, but this still contained traces of bromine and polymerised too rapidly to allow of adequate fractionation. The obvious impurity of this specimen (Found: C, 76·0; H, 11·2. $C_{12}H_{20}$ requires C, 87·8; H, 12·2%) rendered it unsuitable for further use.

The authors desire to acknowledge grants from the Government Grant Committee of the Royal Society and the Chemical Society (to E. H. F. and B. D. L. respectively) which have defrayed a portion of the cost of this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, October 7th*, 1927.]

CCCXCIII.—*The Reactions between Oxygen and Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

A STUDY of the gases occluded in coal that had been exposed to the air for a long time (see Wheeler, J., 1918, **113**, 945) suggested that one reaction between oxygen and coal, or some part of the coal substance, was analogous to that between oxygen and carbon which results in the formation of a physico-chemical complex (Rhead and Wheeler, J., 1913, **103**, 461). Later work (Tideswell and Wheeler, J., 1919, **115**, 895; 1920, **117**, 794) emphasised the analogy by showing that, not only did exhaustion of coal at a slightly higher temperature than that at which "fixation" of oxygen had taken place remove part of the oxygen as oxides of carbon, but also that the coal then had a renewed capacity for attaching oxygen. To explain this "revivification," it was assumed that the molecular structure of that part of coal to which oxygen attaches itself approximated to that of carbon.

We have recently shown (J., 1925, **127**, 112, 2238; 1926, 1410) that the portion of coal most readily attacked by oxygen at low

temperatures is the ulmin portion, the molecular structure of which contains a compact system of 5- and 6-membered rings, which recalls the compact 6-membered ring structure suggested for carbon by Aschan (*Chem.-Ztg.*, 1909, **33**, 561). The analogy between the oxidation of carbon and that of coal is not, however, complete. During the latter, the hydrogen-containing groupings of the ulmin molecule play an important part, whilst stable acidic (carboxylic) groupings are formed which have no counterpart in the composition of the carbon–oxygen complex formed when carbon is oxidised.

In the present research, which should be considered in conjunction with that of Tideswell and Wheeler (*loc. cit.*), whose methods of experiment we have followed, we have studied more particularly the behaviour of the hydrogen-containing groupings of the ulmin molecule during the oxidation of coal, as disclosed by the formation of water. Oxygen was circulated at a constant rate through powdered coal maintained at a constant temperature, and periodic measurements were made of the total quantity of oxygen disappearing and of the quantities of each of the products of reaction. When the reaction became slow, the oxidised coal was heated in a vacuum to a higher temperature (below the temperature of decomposition of the coal-substance), cooled to the original reaction temperature, and oxygen again admitted. This procedure was repeated several times.

The experiments can be divided into two main groups: (1) with newly-won coal, the vitrain portion of the Hamstead (Brazills) seam, Staffs.; and (2) with vitrain from the same seam after it had been transformed into soluble ulmins by prolonged atmospheric oxidation at 150° (see Francis and Wheeler, *loc. cit.*).

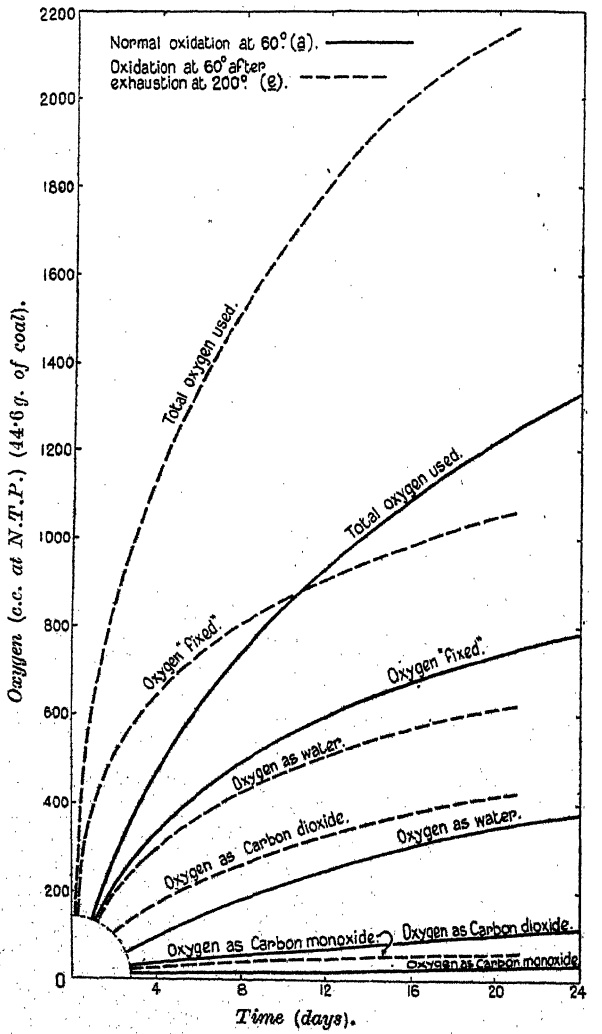
Series I. Experiments with Newly-won Coal.

The coal, ground to pass through a 40- and remain on a 60-mesh sieve (I.M.M. standard), was dried in a vacuum over sulphuric acid during 14 days and introduced into the reaction tube, where it was first heated at 60° in a vacuum and then treated with pure dry nitrogen, which was circulated through the rest of the apparatus. The weight of dry coal used was 44·6 g. The following sequence of experiments was made:

(*a*) Oxidation at 60°.
(*b*) Exhaustion at 100°, followed by oxidation at 60°.
(*c*) Exhaustion at 100°, followed by oxidation at 60°.
(*d*) Exhaustion at 185°, followed by oxidation at 60°.
(*e*) Exhaustion at 200°, followed by oxidation at 60°.
(*f*) Exhaustion at 200°, followed by oxidation at 60°.

The main results are recorded in Tables I and II and in Figs. 1 and 2, all volumes of oxygen and oxygen-equivalents being reduced to *N.T.P.* throughout. The first oxidation (*a*) at 60° can be

FIG. 1.



regarded as the "normal" oxidation of the coal at that temperature. Its general course is shown in curve *a*, Fig. 1.

Carbon dioxide and monoxide were produced from the first at a rate comparable with that of the disappearance of oxygen, but

TABLE I.

Series I. The Oxidation of Newly-won Coal (44·6 g.) at 60°.

Experiment No.	Duration, days.	Oxygen used, c.c.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Oxygen "fixed," c.c.
(*a*) Normal oxidation ...	35	1544	450	169	40	885
(*b*) After exhaustion at 100° (1st)	28	697	122	91	21	463
(*c*) After exhaustion at 100° (2nd)	26	564	105	72	12	375
(*d*) After exhaustion at 185°	17	781	237	127	21	396
(*e*) After exhaustion at 200° (1st)	21	2173	621	423	67	1062
(*f*) After exhaustion at 200° (2nd)	24	1914	461	403	82	968

TABLE II.

Series I. Products of Decomposition of Oxidised Coal.

Experiment.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Total.
At 100° after oxidation *a*	79·8	39·7	3·5	123
At 100° after oxidation *b*	87·0	45·8	4·2	137
At 185° after oxidation *c*	352·0	269·0	39·0	660
At 200° after oxidation *d*	501·0	595·0	81·0	1177
At 200° after oxidation *e*	332·0	634·0	91·0	1057

the appearance of water in the absorption tubes was more gradual. This was no doubt because the coal, being initially dry, retained some of the water vapour first formed. There is no reason to doubt but that the production of water vapour actually corresponded with the production of oxides of carbon during the early stages as it did throughout the rest of the oxidation. As the reaction proceeded, a smaller proportion of the oxygen used became "fixed."

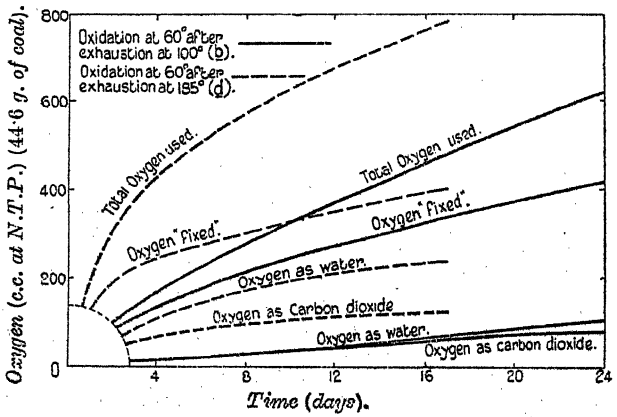
Oxidation was still continuing at a slowly decreasing rate at the end of 35 days, but the experiment was stopped and the apparatus evacuated, the temperature of the coal being raised to 100°. Considerable decomposition of the oxygenated groupings in the coal, equivalent to 123 c.c. of oxygen, occurred (see Table II), 65% of the oxygen thus removed appearing as water, 32·2% as carbon dioxide, and 2·8% as carbon monoxide.

After this exhaustion at 100°, the rate of oxidation at 60° (*b*, Fig. 2) had increased, the "normal" oxidation of the coal being continued, and the oxygen removed from the ulmins by the exhaustion, amounting to about one-seventh of the oxygen fixed during experiment *a*, being simultaneously replaced. Experiment *b* was continued during 28 days, and the coal then again exhausted at

100°. Water and the oxides of carbon were evolved in the same proportions as during the first evacuation, showing that the groupings attacked were of the same character; but rather larger quantities, equivalent to 137 c.c. of oxygen, were obtained owing to the continuance of the "normal" oxidation of the coal.

After this second exhaustion at 100°, the rate of oxidation at 60° (*c*) had again increased, in proportion with the amount of oxygen removed during exhaustion. Estimating, from the oxidation curve for experiment *a*, that during the normal oxidation of the coal the daily fixation of oxygen averaged 12 and 9 c.c. in experiments *b* and *c*, we calculate the fixations consequent on the decompositions at 100° to be 127 and 141 c.c., corresponding with

FIG. 2.



123 and 137 c.c. of oxygen removed during the subsequent decompositions. The oxidation was continued during 26 days and the coal then exhausted at 185°. At this temperature the amount of the "fixed" oxygen released as water and oxides of carbon was considerably greater than at 100°. During experiments *a*, *b*, and *c*, a total of 1723 c.c. of oxygen had become fixed, whilst during the two exhaustions at 100°, 260 c.c. had been released. Of the balance, nearly one-half (660 c.c.) was removed during exhaustion at 185° (see Table II). The proportion of oxides of carbon in the products was greater than at 100°, showing that the character of the groupings decomposed was different.

The rate of oxidation at 60° (*d*) after this treatment was initially very rapid (curve *d*, Fig. 2). This experiment was stopped after 17 days, and the coal then exhausted at 200°. The total amount of oxygen fixed as the result of all the operations up to this point was 1199 c.c. The evacuation at 200° removed as water and

oxides of carbon 1177 c.c., or 98·2%. The proportion of oxides of carbon was greater than at 185°.

Oxidation at 60° (*e*, Fig. 1) was now very rapid. Considerable volumes of oxides of carbon and water were produced from the first, their quantity, in proportion to the amount of oxygen fixed, being greater than in the earlier experiments of the series. After 21 days, 1062 c.c. of oxygen had been fixed, the total amount in the coal being therefore 1084 c.c. (1199 − 1177 + 1062 c.c.). Exhaustion at 200° removed 1057 c.c., or 97·5%. The gases contained a higher proportion of oxides of carbon than those from the previous exhaustion at 200°. Oxidation at 60° (*f*), following this second exhaustion at 200°, was again very rapid. The production of oxides of carbon was greater and that of water was less than in experiment *e*, indicating the gradual elimination of groupings rich in hydrogen.

Series II. Experiments with Coal oxidised at 150°.

The material, 97% of which was soluble in aqueous potassium hydroxide, contained C, 63·8; H, 2·7%. From our previous work, we knew that extensive decomposition of the oxygenated groupings (chiefly carboxylic) of this soluble coal-ulmin would take place on heating in a vacuum. Only 9·76 g. were therefore used for the experiments. The results of a series of oxidations at 60° are recorded in Table III, and those of a series of decompositions at different temperatures in Table IV. No decomposition took place at 100°.

Although during the first oxidation at 60° (*a*), before any heat treatment, some "fixation" of oxygen occurred, there were no gaseous products, and it seems clear that the disappearance of oxygen, half of which occurred whilst it was being admitted into the apparatus, was due to adsorption and solution in the interior of the coal. Exhaustion at 220° caused a partial decomposition of the oxygenated groupings of the ulmin molecule, but the oxygen thus removed, unlike that removed during the corresponding experiments with coal, was not replaced during the subsequent oxidation at 60° (*b*). Physical adsorption of oxygen occurred, whilst there was chemical reaction resulting in the fixation of 4 c.c. of oxygen and yielding traces of oxides of carbon. Possibly water was formed also and retained by the ulmin. Heating at 320° caused considerable decomposition, and, although during the subsequent oxidation at 60° there was appreciable chemical combination with the coal-ulmin, this was by no means as great, having regard to the amount of oxygen previously removed, as might be expected from the results of the experiments with newly-won coal. The

two subsequent exhaustions at 320° (after oxidations *c* and *d*) both caused some decomposition, the volumes of the products being about one-tenth of those yielded during the first exhaustion (after oxidation *b*). These results, and those of the decomposition at 420° and the subsequent oxidation at 60°, emphasise the difference in character between newly-won coal and the soluble coal-ulmin produced from it by oxidation.

TABLE III.

Series II. The Oxidation of Soluble Coal-ulmin (9·76 *g.*) *at* 60°.

Experiment No.	Duration, days.	Oxygen used, c.c.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Oxygen "fixed," c.c.
(*a*) Normal oxidation ...	5	18·4	Nil	Nil	Nil	18·4
(*b*) After exhaustion at 200°	8	22·9	Nil	0·5	Trace	22·4
(*c*) After exhaustion at 320° (1st)	4	53·4	4·4	8·6	8·0	32·4
(*d*) After exhaustion at 320° (2nd)	7	45·4	1·3	4·6	6·0	33·5
(*e*) After exhaustion at 320° (3rd)	5	37·8	Nil	2·1	2·8	32·9
(*f*) After exhaustion at 420°	9	104·4	10·0	12·7	6·4	75·3

TABLE IV.

Products of Decomposition of Soluble Coal-ulmin.

Experiment.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Total.
At 220° after oxidation *a*	60·5	112·5	6·3	179·3
At 320° after oxidation *b*	71·0	381·0	31·0	483·0
At 320° after oxidation *c*	10·6	43·3	5·1	59·0
At 320° after oxidation *d*	14·9	25·0	3·7	43·6
At 420° after oxidation *e*	187·0	420·0	67·5	674·5

We explain the results of the two series of experiments as follows. The oxidation of coal takes place through the medium of an adsorbed layer (compare Tideswell and Wheeler, *loc. cit.*), which almost immediately reacts with certain external groupings of the ulmin molecule, yielding water, carbon dioxide, and carbon monoxide, and forming unstable oxygenated groupings at the points of attack. As the adsorbed layer enters into chemical combination with the coal, it is replaced by a fresh layer, the process being continuous so long as there are groupings remaining with which oxygen can combine at the temperature of experiment. The unstable oxygenated groupings formed are ultimately carboxylic in character and cause the coal-ulmin to become soluble in alkalis.

When the temperature of the coal is raised under vacuum, the oxygenated groupings that have been formed are decomposed, yielding water and the oxides of carbon, the oxygen contained in these being equal in quantity to that "fixed" during the oxidation. The coal now has an increased capacity for retaining oxygen, beyond that due to the normal oxidation, commensurate with the amount removed during exhaustion.

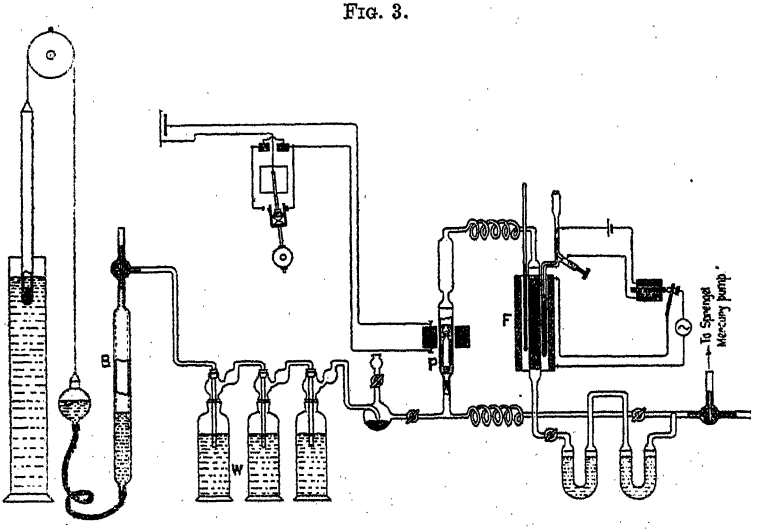
This process of revivification can be repeated many times, but the character of the products of decomposition at each successive exhaustion gradually changes, because groupings of slightly different character are attacked or decomposed. During exhaustion, suitable groupings near those to which oxygen has become attached furnish the hydrogen and carbon required to yield the water and oxides of carbon evolved. During the earlier exhaustions, water is the chief product of decomposition, the action being akin to dehydration. This may result in the formation of internal anhydrides from neighbouring carboxyl groupings, of lactones from suitably placed carboxyl and hydroxyl groups, or of unsaturated groupings such as are produced on the dehydration of β-hydroxy-acids. The number and type of the groupings that can be attacked depend upon the temperature at which oxidation is effected. Oxidation at 60°, as in the series of experiments with newly-won coal, is limited; but at 150°, the temperature employed to produce from that coal the soluble ulmins used for the second series of experiments, all the external groupings of the molecule are eventually attacked, leaving oxygenated (chiefly carboxylic) groupings in their place. No suitable groupings are available in such a fully-oxidised coal for the type of decomposition, permitting almost complete revivification, that obtains with a partly oxidised coal, but the decomposition (at the high temperature required) modifies the ulmin molecule profoundly, leaving a comparatively stable residue, there being but few groupings containing oxygen and hydrogen. Such revivification of this residue as can be effected is of the same character as is obtainable with carbon, and it is probable that the molecular structure of the residue approximates to that of carbon. With coals saturated with oxygen at temperatures between 60° and 150°, different degrees of revivification, by exhaustion at a higher temperature than that of oxidation, are possible.

Experimental.

The circulation apparatus employed for submitting the coal to the action of oxygen differed in many respects from that used by Tideswell and Wheeler (*loc. cit.*). The reaction tube in which the powdered coal was packed was supported vertically within an

electrically-heated furnace (F, Fig. 3), the temperature of which could be maintained constant by means of an electric thermostat. The lower end of the reaction tube was connected by ground-glass joints to two weighed U-tubes in series. The first contained granular calcium chloride for the absorption of water, and the second, asbestos impregnated with sodium hydroxide (the top of each limb being covered by a layer of granular calcium chloride) for the absorption of carbon dioxide. These U-tubes were duplicated so that they could be periodically removed for weighing and fresh ones substituted.

FIG. 3.



Circulation of the oxygen through the coal and absorption tubes was effected by an electrically-operated glass pump, P, of special construction (see Francis, *Fuel*, 1926, 5, 39). The oxygen entering the apparatus was first dried by bubbling through shallow layers of concentrated sulphuric acid contained in a series of large wash-bottles, W, and then passed through a mercury seal of about 1 mm. The charges of oxygen required for an experiment were contained in a graduated burette, B, over a mixture of equal parts by volume of glycerol and water. The reservoir of this burette was supported by a cord which passed over a pulley to a counterweight consisting of a tube, containing mercury, which dipped into a deep jar containing glycerol and water. The external diameter of the counterweight was equal to the internal diameter of the burette, so that as the level of the liquid in the burette rose, consequent on absorption of oxygen by the coal, the reservoir rose an equal amount and the pressure was maintained constant. The pressure was adjusted at

the beginning of an experiment to be just sufficient to force the oxygen through the layers of sulphuric acid and the mercury seal.

As absorption by the coal proceeded, oxygen was drawn into the apparatus to maintain a constant pressure. The volume thus entering was measured periodically on the burette. Corrections were made for variations in atmospheric temperature and pressure and for the vapour pressure of the liquid in the burette. The oxygen, which was prepared by the action of a solution of potassium permanganate on a mixture of hydrogen peroxide and dilute sulphuric acid, was of 99·5% purity. Simultaneously with the measurements of the oxygen used, the weights of water and carbon dioxide formed were determined from the increase in weight of the U-tubes, and a sample of the circulating gases was analysed to determine the amount of carbon monoxide formed.

At the conclusion of an oxidation experiment, the apparatus was rapidly evacuated and the coal then raised to the required temperature during 30 hours, the gases evolved being drawn, by means of a Sprengel mercury pump, through the weighed U-tubes. Water and carbon dioxide were thus absorbed and estimated, and carbon monoxide was collected and measured.

The work described in this paper forms part of a research on the spontaneous combustion of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish it.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, September 19th*, 1927.]

CCCXCIV.—*The Ternary Systems Copper Acetate–Acetic Acid–Water and Lead Acetate–Acetic Acid–Water at* 25°.

By KARL SANDVED.

IN connexion with a study of the relation between lead chloride and lead acetate in aqueous solution, the system lead acetate–acetic acid–water was examined, and also, for the sake of completeness, the system copper acetate–acetic acid–water. The results form the subject of the present communication.

The acetate–acetic acid–water systems investigated previously are of the same general type (Sodium salt: Dukelski, *Z. anorg. Chem.*, 1909, **62**, 114; Dunningham, J., 1912, **101**, 431. Ammonium salt: Ruth Sugden, J., 1926, 960. Silver salt: Knox and Will, J., 1919, **115**, 853), all obeying the following two rules: (1) The

solubility of the acetate is depressed on addition of acetic acid, as would be expected from the classical solubility laws; (2) acid acetates occur in the solid phase at a certain concentration of acetic acid.

Of the systems described in the present communication, the copper acetate system conforms completely to these rules, whereas the lead acetate system shows a totally different behaviour. The exceptional complexity of lead acetate solutions has frequently been described. A complete investigation of the ternary system lead acetate–acetic acid–water throws some light upon the constitution of these solutions, and provides data bearing on the existence or non-existence of acid lead acetates, which have not hitherto been described.

Experimental.

Copper Acetate–Acetic Acid–Water at 25°.

The following neutral and acid salts have been described: $Cu(C_2H_3O_2)_2$ (Tilden, J., 1884, **45**, 266), $Cu(C_2H_3O_2)_2,H_2O$ (Gerhardt, *J. Pharm.*, 1845, **9**, 50), $Cu(C_2H_3O_2)_2,5H_2O$ (Wöhler, *Pogg. Ann.*, 1836, **37**, 166; Astre, *J. Pharm. Chim.*, 1893, **28**, 542), $Cu(C_2H_3O_2)_2,2HC_2H_3O_2,H_2O$ (Villiers, *Compt. rend.*, 1877, **85**, 1236).

The mixtures were shaken in a thermostat at 25° ± 0·05°. The equilibria were completely established in 5 to 6 hours, except in solutions containing more than 90% of acetate, which required about 24 hours. The solid was allowed to settle, and the clear solution was drawn off and analysed. The solid was then rapidly drained on a Buchner funnel and analysed, the composition of the dry solid being found by Schreinemakers's method (*Z. physikal. Chem.*, 1893, **11**, 81). Copper was estimated by electrolytic deposition from dilute sulphuric acid solution (see Fischer, *Z. angew. Chem.*, 1907, **20**, 134), whilst the total acetic acid was estimated by distillation with phosphoric acid, as described by Dukelski (*loc. cit.*).

The copper acetate used was the purest obtainable from British Drug Houses, Ltd. Estimations of copper and acetic acid were in accord with the formula $Cu(C_2H_3O_2)_2,H_2O$. The anhydrous acetate was prepared by heating the monohydrate for 5 hours at 95—100° (Angel and Harcourt, J., 1902, **81**, 1385; Tilden, *loc. cit.*). Analysis then gave Cu, 34·9, 34·8, 34·9, 34·91, 34·9 (mean, 34·9) [Calc.: Cu, 35·0%]. This anhydrous copper acetate was employed for solutions corresponding to the extreme right side of the diagram.

The experimental results are in Table I, and Fig. 1 shows the corresponding graph, constructed according to Lodočnikow's method (*Z. anorg. Chem.*, 1926, **151**, 181). If, in order to show more clearly the varying composition of the saturated solutions, the scale is

increased ten times (see right-hand ordinates), the broken line in Fig. 1 is obtained. It is seen that three compounds are capable of existence, *viz.*, (1) $Cu(C_2H_3O_2)_2,H_2O$ (marked 1 in the figure); (2) $Cu(C_2H_3O_2)_2,HC_2H_3O_2,H_2O$ (marked 2); (3) $Cu(C_2H_3O_2)_2,HC_2H_3O_2$ (marked 3).

FIG. 1.

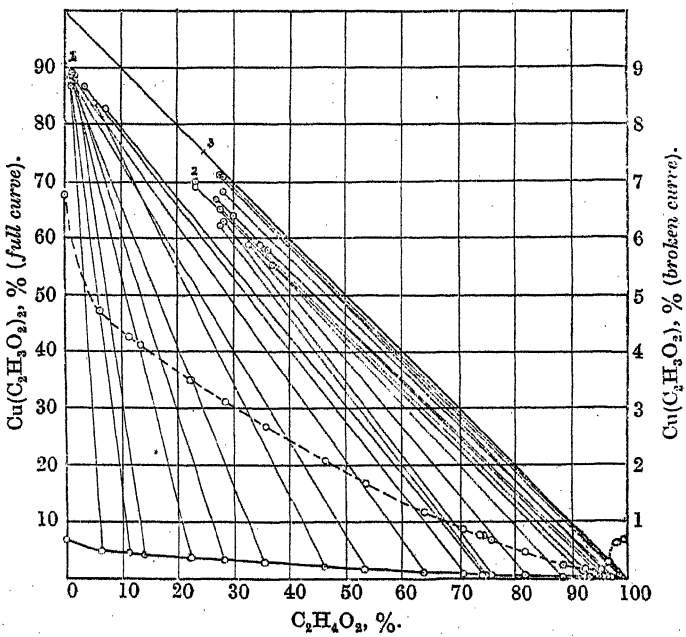


TABLE I.

The Ternary System $Cu(C_2H_3O_2)_2$–$HC_2H_3O_2$–H_2O at 25°.

Liquid.		Wet solid.		Liquid.		Wet solid.	
%$CuAc_2$.	%HAc.	%$CuAc_2$.	%HAc.	%$CuAc_2$.	%HAc.	%$CuAc_2$.	%HAc.
6·79	—	76·02	0·09	0·69	75·74	62·95	28·12
4·73	6·18	88·32	0·82	0·48	81·60	58·87	32·57
4·27	11·14	86·70	1·03	0·25	88·46	65·11	27·96
4·16	13·65	89·31	1·04	0·22	92·17	55·45	36·97
3·49	22·35	87·85	1·64	0·21	93·33	63·87	29·96
3·12	28·43	88·62	1·57	0·20	94·94	59·04	34·81
2·68	35·53	87·53	0·94	0·21	95·26	66·68	26·67
2·10	46·08	83·70	5·10	0·17	95·40	35·94	58·09
1·70	53·35	88·00	1·81	0·23	95·66	69·01	23·30
1·18	63·67	88·31	0·93	0·23	96·37	71·50	27·49
0·89	70·81	86·60	3·45	0·31	97·20	68·25	28·10
0·79	74·06	82·90	7·20	0·71	98·77	70·91	28·31
0·77	74·42	62·10	27·59	0·71	98·91	70·58	28·01

The ternary invariant point between (1) and (2) lies at 0·79% $Cu(C_2H_3O_2)_2$ and 74·06% $HC_2H_3O_2$, and that between (2) and (3)

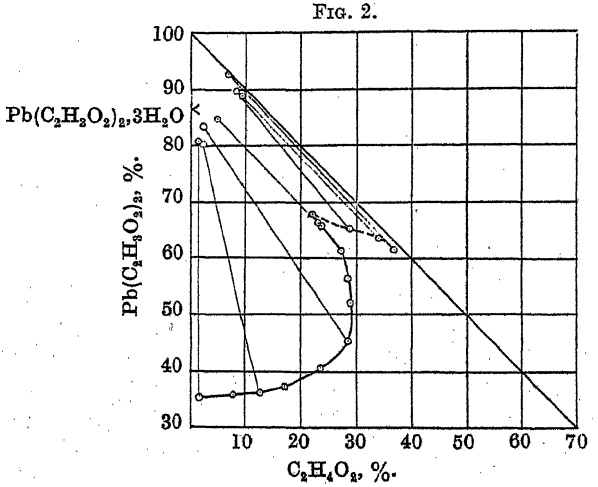
0·17% $Cu(C_2H_3O_2)_2$ and 95·40% $HC_2H_3O_2$. The solubility of copper acetate in water at 25° is 6·79%.

The pentahydrate described by Wöhler and by Astre (*locc. cit.*) is not stable as a solid at 25°. Fig. 1 shows, moreover, that the acid salts obtained are not of the same type as that described by Villiers (*loc. cit.*), for no acid salt is indicated containing more than 1 mol. of acetic acid to 1 mol. of copper acetate.

Lead Acetate–Acetic Acid–Water at 25°.

Numerous basic and neutral lead acetates are mentioned in the literature, whereas no acid compound has been identified (Gmelin-Kraut, "Handbuch," 1924). Sakabe (*Mem. Coll. Sci. Kyoto*, 1914,

FIG. 2.



1, 57) has investigated the system lead oxide–acetic acid–water, but his data do not go beyond 19·28% of free acid. Moreover, his figures do not agree either with the results of the present work or with those obtained by Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2346) for the system lead acetate–lead oxide–water. Thus Sakabe found the solubility of lead acetate to be about 6·5%, whereas the true solubility is about six times as high. Further, Sakabe employed ignited lead oxide for his experiments and probably true equilibria were not attained owing to the inactivity of the oxide.

The lead was estimated as sulphate according to the recognised method. For the estimation of acetic acid, an excess of *N*/5-sulphuric acid was added to the solution, which was then diluted with twice its volume of alcohol and titrated with *N*/5-sodium hydroxide (free from carbon dioxide) and phenolphthalein. (The addition of alcohol produced a very sharp end-point.) Boiled

water only was used, and all flasks were fitted with tight glass stoppers. In order to check the method, titrations were carried out with pure lead acetate from the British Drug Houses: the alkali required for back titration was always equivalent to the amount of acid added. Anhydrous lead acetate was prepared by heating the trihydrate at 130°. Three estimations of lead in the dried product gave 63·7, 63·7, 63·7 [Calc.: Pb, 63·7%].

As may be seen from Table II and Fig. 2, the solubility of lead acetate increases on addition of acetic acid, at first rather slowly, but from 20% acetic acid very sharply. The maximum percentage of acetic acid is at 28·99%, which consequently is the highest possible content of acetic acid in presence of lead acetate trihydrate as a solid at 25°, owing to the high solubility of the latter. By dissolving the trihydrate in glacial acetic acid, a point was finally reached corresponding to 67·90% $Pb(C_2H_3O_2)_2$ and 22·01% $HC_2H_3O_2$, marked * in Table II. Anhydrous lead acetate was used

TABLE II.

Liquid.		Wet solid.		Liquid.		Wet solid.	
$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.
35·50	1·61	80·80	1·35	61·48	27·10		
35·62	7·82			65·84	23·62	84·63	4·87
36·08	12·56	80·05	2·39	66·48	22·98		
37·10	17·04			*67·90	22·01		
40·58	23·58			65·09	28·90	89·85	8·05
45·39	28·55	83·39	2·73	63·55	34·00	88·70	9·28
52·10	28·99			61·50	36·77	92·61	6·81
56·50	28·41						

for the extreme part of the diagram; it dissolved very slowly in concentrated acid, 2 days being necessary for the attainment of constant values. The solution always showed a slight turbidity, which rendered separation of the two phases impossible at the highest concentrations of acid. This part of the curve, being less trustworthy, has been drawn as a broken line in Fig. 2, but it nevertheless shows that anhydrous lead acetate is still present as a solid and that no acid compounds can be prepared in this way. In order to check this result, the anhydrous salt and glacial acetic acid were boiled together for 5 hours, but the high viscosity and density of the solution prevented the separation of the solid from the liquid. The appearance of the solution was not perceptibly altered after 3 weeks, and it was quite impossible to effect any crystallisation in this highly supersaturated solution. It may be emphasised that these experiments do not definitely prove the non-existence of acid lead acetates. The velocity of reaction in such viscous systems is so depressed that true equilibria may not be reached.

Discussion.

The abnormal behaviour of lead acetate solutions has been long known. Measurements of electrolytic conductivity (Noyes and Whitcomb, *J. Amer. Chem. Soc.*, 1905, **27**, 747) and of *E.M.F.* (Conrad, Diss., Göttingen, 1903) indicate a low concentration of free lead ions in these solutions : according to Noyes and Whitcomb the degree of dissociation in *N*-solution is about 17%.

These results are in agreement with the changes which occur when lead salts and acetates are brought together. The increased solubility of lead sulphate in ammonium acetate (Carius, *Annalen*, 1863, **125**, 87) is explained by Noyes and Whitcomb as due to the formation of un-ionised lead acetate by metathesis; and a similar assumption was made by Fox (J., 1909, **95**, 878) to account for the solubility of lead sulphate in alkali acetate solutions.

Several other authors have maintained, however, that various other factors, besides the low degree of dissociation, have to be considered in such solutions. White (*Amer. Chem. J.*, 1904, **31**, 4; 1906, **35**, 218) explains the increased solubility of lead chloride in lead acetate solutions, as well as the type of double compound isolated, by assuming complex ions to be present in the solution. (The author hopes to publish the results of a phase-rule study of this system.)

Further evidence on the existence of complex ions has been given by Blomberg (*Chem. Weekblad*, 1914, **11**, 1030; *Z. Elektrochem.*, 1915, **21**, 438), Conrad (*loc. cit.*), and Labendzinski (Diss., Breslau, 1904). By postulating the equilibria

(1) $2Pb(C_2H_3O_2)_2 \rightleftharpoons Pb(C_2H_3O_2)^{\cdot} + Pb(C_2H_3O_2)_3'$
(2) $Pb(C_2H_3O_2)^{\cdot} \rightleftharpoons Pb^{\cdot\cdot} + C_2H_3O_2'$
(3) $Pb(C_2H_3O_2)_3' \rightleftharpoons Pb(C_2H_3O_2)^{\cdot} + 2C_2H_3O_2'$

Blomberg is able to account for the abnormal solubility data as well as for the electrochemical measurements referred to previously.

As shown by Hill (*J. Amer. Chem. Soc.*, 1917, **39**, 218), the conditions are altogether different when acetic acid is used instead of alkali acetates; thus, the solubility of lead chloride increases slightly on addition of small amounts of acetic acid, and then falls regularly on further additions (see Herz and Martin, *Z. anorg. Chem.*, 1924, **140**, 339). Hill points out that the theory of metathesis predicts an increase of solubility and therefore can hardly be valid; he suggests, furthermore, that the grounds for these anomalies lie in deviations from the mass-action law. Experiments carried out in connexion with the present work show that the solubility of lead sulphate is depressed in a similar way on addition of acetic acid.

It seems evident, however, that these facts do not by any means

disprove Noyes and Whitcomb's hypothesis. All the data available on lead acetate solutions show that this salt, even when regarded as a ternary electrolyte, is more extensively dissociated than acetic acid. Hence the equilibrium $PbCl_2 + 2HC_2H_3O_2 \rightleftharpoons Pb(C_2H_3O_2)_2 + 2HCl$ will give very small amounts of lead acetate in the solution. The slight formation of lead acetate is, however, probably the cause of the increased solubility on the first part of Hill's curve.

When strong electrolytes such as alkali acetates are used instead of acetic acid, the conditions are evidently completely altered, and in this case the acetate ions will have to unite with the lead ions to a considerable extent. In the author's opinion, the increased solubility of sparingly soluble lead salts in solutions of alkali acetates is chiefly due to this combination of ions. It does not appear reasonable that this reaction leads to the formation of undissociated lead acetate only, as originally supposed by Noyes and Whitcomb, but rather to univalent ions $Pb(C_2H_3O_2)^{\cdot}$. By considering lead acetate as a binary electrolyte, it is possible to interpret more satisfactorily the results obtained from conductivity measurements. The degree of dissociation calculated on this assumption is about 70% in *N*-solutions, giving the maximum upper limit of this primary dissociation. The measurements by Conrad (*loc. cit.*) seem to show that the second dissociation takes place only to a slight extent.

Fox (*loc. cit.*) gives the following solubilities of lead acetate in potassium acetate solutions at 25° :

$KC_2H_3O_2$, %	0	13·87	15·40	
$Pb(C_2H_3O_2)_2$, %	35·90	38·05	36·91	

Data for the solubility in sodium acetate solutions at 25° have now been obtained :

$NaC_2H_3O_2$, %	0	4·81	15·37	15·96
$Pb(C_2H_3O_2)_2$, %	35·75	35·23	43·28	38·85

If these figures are compared with those in Table II, it will be seen that alkali acetates and acetic acid have approximately the same effect upon the solubility of lead acetate. In the former case, however, the maximum solubility will be reached at a comparatively low concentration of alkali acetate due to changes in the solid phase It will be seen also that the first addition of sodium acetate causes the solubility to fall slightly, while an increase occurs on further addition. This fact seems to be satisfactorily accounted for by the theory of Blomberg (*loc. cit.*). The first quantity of sodium acetate will depress the dissociation of the $Pb(C_2H_3O_2)^{\cdot}$ ion (2), whereas at higher concentrations of acetate ions, and consequently of $Pb(C_2H_3O_2)^{\cdot}$ ions, the formation of complex ions, $Pb(C_2H_3O_2)_3'$, and undissociated molecules (1 and 3) will be predominant. In the case

of acetic acid, the first effect due to the increase in acetate ions will naturally disappear, causing the solubility to increase continuously throughout the whole range.

The extraordinary solubility of lead acetate in acetic acid can hardly be accounted for in any other way than by assuming the occurrence of molecular changes. Differences in the thermodynamical and electrical properties of water and acetic acid (Webb, *J. Amer. Chem. Soc.*, 1926, **48**, 2263) scarcely suffice to explain deviations of the observed magnitude, nor does it seem that the basic character of lead acetate solutions can be of essential importance (Löfman, *Z. anorg. Chem.*, 1919, **107**, 241). Webb (*loc. cit.*) has pointed out that strong electrolytes, such as lithium iodide or nitrate, most probably are incompletely dissociated in glacial acetic acid. It seems therefore plausible to assume that complex salts of the type $x\mathrm{HC_2H_3O_2},y\mathrm{Pb(C_2H_3O_2)_2}$ would be almost undissociated in concentrated acetic acid solution. The failure to isolate any acid salts from these solutions points to a very high solubility of the complex compounds, as may be expected from the modern theories on solubility. A symmetrical combination of the type $\mathrm{AcPbAc}_{\mathrm{Ac}}^{\mathrm{Ac}}$, in which the lead atom is entirely surrounded by acetate groups, will show in respect to its electrical and thermodynamical properties a close similarity to pure acetate groups, and hence have a special ability for penetrating a field built up by such groups.

Summary.

The two ternary systems copper acetate–acetic acid–water and lead acetate–acetic acid–water have been investigated at 25°. The first system belongs to the same type as the alkali acetate–acetic acid–water systems, whereas the second shows totally different properties, in accordance with the generally abnormal character of lead acetate solutions.

It is suggested that this abnormal behaviour is best accounted for by the assumption of molecular changes, and it is pointed out that the supposed non-validity of the mass-action law is insufficient to explain deviations of the observed magnitude.

The author's thanks are due to the Ramsay Memorial Fellowship Trust for placing a fellowship at his disposal, and to Professor J. C. Philip, F.R.S., under whose interested and valuable direction this research was conducted.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, October 21st*, 1927.]

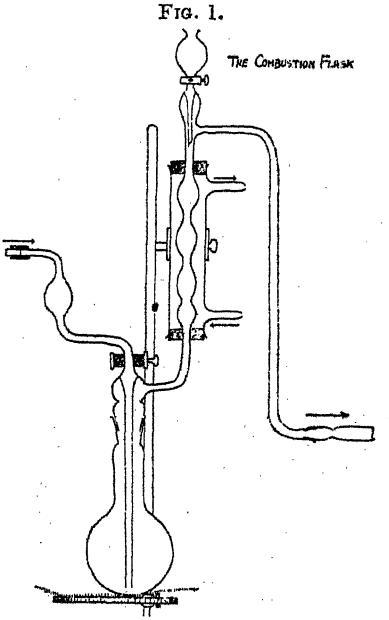
CCCXCV.—*The Determination of Total Carbon and Carbon Dioxide in Small Quantities of Soil Solutions.*

By Colin Falconer Flint.

During the course of a research on the ultimate composition of the soil solution, a method was needed for the determination of total carbon, which was present to the extent of 100—1000 parts per million parts whilst the quantity available for a determination was usually less than 10 c.c. The ordinary permanganate oxidation method used in water analysis did not yield concordant results.

The wet combustion method used in steel analysis (see Corleis, *Stahl u. Eisen*, 1894, **14**, 581; Treadwell–Hall, "Analytical Chemistry," vol. 2, 5th ed., p. 399, New York, 1919) was adapted to the routine examination of soil solutions containing nitrate and chloride as high as 3000 parts of NO_3 and 800 parts of Cl per million. This was achieved by using in the combustion-furnace tube a 6-inch cylinder of reduced copper gauze together with either copper oxide and a spiral of silver gauze or an 8-inch cartridge of lead chromate (see Thorpe and Whiteley, "Manual of Organic Chemical Analysis," London, 1926). The method was then used in the routine examination of a large number of soil solutions for total carbon, and a part of the apparatus was further adapted to the determination of carbon dioxide.

Fig. 1.



Experimental.

(1) *Total Carbon.*—The train of apparatus employed was as follows, in the order indicated: A soda–lime tower, a set of 3 potash bubblers, the combustion flask (Fig. 1) attached through a ground joint to the hard glass combustion tube heated in a light Dennstedt furnace, a sulphuric acid bubbler, a glass-stoppered U-tube containing pumice soaked in sulphuric acid, and glass-stoppered absorption and trap tubes, charged with "Sofnolite" or soda–lime and

topped with calcium chloride. Proper attention was directed to sieving the charges for these tubes and to regulating the speed of the air current; otherwise, fine dust was swept out, causing serious losses. A current of 4 bubbles a second in the bubbler was the fastest consistent with safety, and was used throughout, being regulated by a screw clip before the pumice tube.

50 C.c. of water, 15 c.c. of saturated pure chromic acid solution, and 120 c.c. of pure sulphuric acid were boiled gently in the combustion flask for 10 minutes with the tap-funnel open. The chromate cartridge was then heated to dull redness while a current of purified air was drawn through the apparatus for 20 minutes, the flask being allowed to cool. Next, the tap on the pumice tube was closed, the freshly reduced copper spiral was inserted and heated over a faintly luminous flame that just touched the trough, and the absorption and guard tubes were placed in position. The soil solution was placed in the tap-funnel and drawn into the system, admission of air being avoided, and the funnel was rinsed with a few drops of water. The air current was started again, and the flask boiled over a small flame for 1½ hours. The pumice tube was then closed, the tap-funnel opened, and the absorption tube removed and weighed.

If the initial boiling-out had not been carefully performed, the evolution of gas from the combustion mixture was frequently so rapid as to blow the mixture back into the potash bulbs; this could be controlled to some extent by removing the burner and fanning the flask.

The following figures for blank determination and determinations of total carbon in a standard sugar solution and a soil extract are typical of the results obtained.

The method was tested on sucrose in an apparatus having rubber connexions to the furnace, instead of ground glass joints, and both with and without a reflux condenser. 10 C.c. of sugar solution, containing carbon equivalent to 27·7 mg. of carbon dioxide, and 5 mg. each of NO_3 and Cl, gave 27·2 mg. of carbon dioxide (without reflux) and 28·0 mg. (with reflux); 20 c.c. of liquid gave 55·6 mg. of carbon dioxide. This apparatus, as well as that shown in Fig. 1, gave less than 0·1 mg. increase in weight in blank determinations with the reagents when as much as 0·1 g. of potassium nitrate and 0·05 g. of potassium chloride were used. With the apparatus figured, 5 c.c. of a certain soil solution gave 1·6 mg. of carbon dioxide consistently.

Good agreement was obtained in repeated tests. The errors did not exceed 0·3 mg. with the largest quantities of carbon, which in general yielded 1—30 mg. of carbon dioxide.

(2) *Carbon Dioxide.*—The apparatus was adapted to the deter-

mination of carbon dioxide by cutting the horizontal delivery tube about 1 inch from the reflux condenser and connecting it to the drying and absorption train by means of a rubber joint. To prevent bumping in the solution on boiling, hydrogen was liberated by the action on aluminium of the hydrochloric acid with which the solution was acidified; this metal was chosen for its freedom from surface contamination of carbonate or sulphide. Very dilute acid was used in order to avoid a too rapid evolution of gas. The complete expulsion of carbon dioxide from the system was accelerated by the current of air and the generation of hydrogen, but boiling was continued for 1½ hours as an additional precaution.

100 C.c. of water and 5 c.c. of hydrochloric acid were boiled for 20 minutes in the current of air after ½ inch of 16-gauge aluminium wire had been placed in the exit tube from the reflux condenser; without stopping the boiling, the pumice tube was closed to allow the absorption and guard tube to be inserted; the sample of the soil solution was drawn into the system, and the wire was dislodged from its position and caused to fall into the mixture. (This procedure avoided all danger of "blowing back.") The boiling was continued for 1½ hours, then the absorption tube was weighed.

Since blank determinations gave less than 0·1 mg. increase in weight of the absorption vessels, this method was applied to soil solutions, 10 c.c. being used for each test. With soil solutions of $p_H < 7$, the total carbon dioxide so found did not exceed a few parts per million.

During the publication of this work, a method was described (Nicloux, *Bull. Soc. Chim. biol.*, 1927, **9**, 639) for the rapid and accurate determination of a maximum of 3 mg. of carbon present as organic matter in 1 c.c. of aqueous solution. The chromic–sulphuric acid oxidation takes place in a vacuum, and is catalysed by silver chromate. A method for the micro-determination of carbon dioxide was also described (*ibid.*, p. 758).

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W. 7.

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CCCXCVI.—*The Critical Temperatures of Boron Trichloride and Silicon Tetrachloride.*

By THOMAS WALLACE PARKER and PERCY LUCOCK ROBINSON.

AN investigation involving the determination of critical temperatures is in progress in this laboratory, and these results are submitted because no previous determination appears to have been made in

the case of boron trichloride, whilst the only one relating to silicon tetrachloride is that of Mendeléev (*Annalen*, 1861, **119**, 11). Carefully purified material has been used in each case, and the thermometers have been standardised at or very near to the readings actually used by the National Physical Laboratory, so that considerable trust may be placed in these values.

EXPERIMENTAL.

Preparation of Materials and Filling of Tubes.—The Durosil glass-ware used in these operations was cleaned by treatment with chromic–nitric acid mixture, well washed with numerous changes of water, the last portions being good distilled water, and with alcohol and ether, after which it was dried by heating to 110° in an electric oven.

Boron trichloride. About 120 c.c. of boron trichloride, which had been used for an approximate determination of density (see Briscoe, Robinson, and Smith, this vol., p. 284) and had remained sealed under vacuum in a container provided with a special joint, constituted the initial material for this work. This liquid was subjected to two successive fractional distillations in a vacuum, head and tail fractions of about 5 and 10 c.c. respectively being rejected on each occasion, and the main fractions being received into vessels having special joints. The fractionations were performed with the usual precautions taken in this laboratory and described elsewhere for ensuring the absence of leaks in the train, of moisture on the interior surface of the vessels, and of residual air. The vessel, L, containing the main fraction (90 c.c.) was now attached to the train illustrated in Fig. 1; B_1—B_8 represent the various critical-temperature tubes, with walls 1 mm. thick and bore 4—5 mm., and provided with the thickened capillaries necessary for sealing off under a vacuum; M is the surface-tension vessel previously described (Mills and Robinson, this vol., p. 1823); and N is a vessel with a special joint for receiving the surplus material. This train was evacuated and slowly refilled with dry air 6 times while at 150°, to ensure careful drying, and was sealed off from the pump under the highest vacuum attainable. The special joint was then broken, and the liquid was distilled, solid carbon dioxide–ether being used as refrigerant, into tubes B_1, B_2, and B_3; M was then filled to the requisite level and removed; next, B_4, B_5, B_6, and B_7 were filled and removed in the order indicated, and, the major portion of the residual liquid having been distilled into N, which was drawn off, B_8 was filled and removed. The normal procedure in charging the critical-temperature tubes was

to fill them with liquid and then distil back to the main bulk until the desired quantity remained in the tube, the final sealing being done without arrest in the backward flow of vapour. It could thus be reasonably presumed that the tubes contained only the slightest trace of air, if any at all.

Silicon tetrachloride. The material used was the head fraction of silicon tetrachloride obtained from the second vacuum distillation of the U.S.A. sample (see Robinson and Smith, J., 1926, 1272) and was considered of sufficient purity for immediate use. A train

FIG. 1.

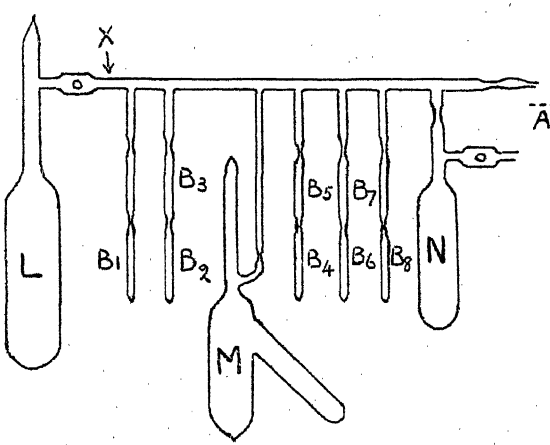
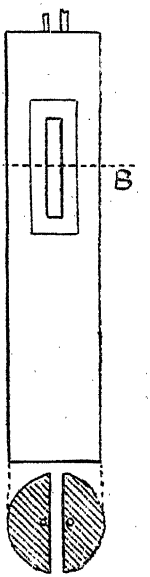


FIG. 2.



Elevation and Section through AB.

similar to Fig. 1 was employed. A head fraction of 2 c.c. was first taken in N, tubes B_1, B_2, B_3, and B_4 were successively filled and removed, and then M was filled. As described elsewhere (Mills and Robinson, *loc. cit.*), when M had received sufficient liquid a fracture occurred in the special joint of L and this vessel was at once drawn off at X, the apparatus was immediately attached to the pump at B_8, rapidly evacuated, and sealed off above this point, after which M was removed. This unfortunate accident rendered it impossible to fill further tubes.

Critical-temperature Apparatus and Phenomena.—Apparatus. This was a modification of that of Hackspill and Mathieu (*Bull. Soc. chim.*,

1919, 25, 482). A cylinder of copper (Fig. 2), 5 cm. × 27 cm., with a central hole 11 mm. in diameter and two other holes 7 mm. in diameter and reaching almost to the bottom, was constructed for us in the Department of Engineering by the courtesy of Prof. C. J. Hawkes. The metal between the outer and the central holes was 2 mm. at the thinnest parts. A window, 4 cm. high and the width of the central hole, was cut completely through the metal about 10 cm. from the top. This window was closed by thick sheets of colourless mica, bound in position by means of copper wire. The critical-temperature tube was placed in the central hole, and rested on a length of glass rod at a height convenient for observation. The thermometers were similarly supported in the side holes, so that the bulbs were level with the middle of the critical-temperature tube, correction for exposed stem being made when necessary. The apparatus with the tube and thermometers in position was placed inside a heater (kindly lent to the authors by Dr. L. A. Sayce) consisting of a sheet-copper cylinder 22 in. × 6 in., fitted on opposite sides with vertical glass windows 1 in. wide, and heated by a spiral winding of nichrome wire insulated from the copper by a layer of asbestos board. The bottom was well lagged and a lid of several thicknesses of asbestos board closed the top. This arrangement, used with suitable external resistances, was found to change the temperature of the metal cylinder very slowly and uniformly, while tests made by changing the thermometers from hole to hole showed that under the conditions prevailing during the experiments, a difference in temperature of less than ± 0·1° was to be expected in the three positions.

Phenomena. Young (*Phil. Mag.*, 1906, **20**, 803) and Travers and Usher (*Proc. Roy. Soc.*, 1906, **78**, 247) seem to have found the phenomena attending the change of state susceptible of much sharper observation than did Hackspill and Mathieu (*loc. cit.*), who state that it is difficult to observe the critical phenomena to less than ± 1·0°. The present authors, in common with most observers, have taken the temperature recorded at the appearance of the meniscus in the cloud during the change from vapour to liquid as the critical temperature. This phenomenon was observed against a bright background, and as there was an easily perceptible change during a fall of 0·2°, it is probable that the individual readings for identical conditions of the cloud were within ± 0·1° of the actual temperature. This is probably much beyond the constancy to be expected in the temperature at which identical appearances occur in separate experiments. Tubes filled to the extent of one-third of their volume gave the most satisfactory critical phenomena. The results are in the table.

Liquid.	Tube.	Successive observations at same heating.						Mean.
BCl_3	B_2	178·8°	178·7°	178·7°				178·7°
	B_4	178·9	178·9	178·8				178·9
	B_5	178·7	178·7	178·7				178·7
	B_6	178·9	178·8	178·7				178·8
$SiCl_4$	C_2	233·5	233·5					233·5
	C_3	233·6	233·5	233·5				233·5
	C_4	233·9	233·8	233·8	233·6°	233·6°	233·5°	233·7

The results for boron trichloride do not indicate any real difference from tube to tube, and give a mean value 178·8° ± 0·2°, but they do show that there is a tendency for the value to fall if the material is maintained at or about the critical temperature for some time. Two days before the determinations for B_2 given above, the tube was accidentally heated to 210° and then gave two successive results of 178·4°. There is some reason to suppose that the regular differences in the critical temperature observed in successive heatings, although not much greater than the probable experimental error, may in fact be real. If so, it appears that heating the liquid to a higher temperature causes a depression of the critical temperature which may be due to a change in the physical properties of the liquid, but which, in the opinion of the authors, is not caused, in the case of a compound such as boron trichloride, by thermal dissociation. Similar differences are shown in the case of silicon tetrachloride, particularly in tube C_4. The mean value of the critical temperature is 233·6° ± 0·2°, which is rather higher than that due to Mendeléev (*loc. cit.*).

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, August 5th*, 1927.]

CCCXCVII.—*The Complex Cyanides of Molybdenum.*

By WILLIAM RALPH BUCKNALL and WILLIAM WARDLAW.

SPECIAL interest is attached to the complex cyanides of molybdenum and tungsten, $R_4Mo(CN)_8$ and $R_4W(CN)_8$, for few cyanides of quadrivalent elements exist, and complex cyanides are known only in isolated cases. Moreover, these complex salts represent well-substantiated examples of a co-ordination number of 8, and the exceptional stability of the complex ions $[Mo(CN)_8]''''$ and $[W(CN)_8]''''$ finds a satisfactory explanation in the modern electronic theory of valency. Undoubtedly this marked stability is intimately associated with the fact that the cyanide units are regularly distributed round a central metallic atom, of which the effective atomic number—in the case of molybdenum, 54, and of tungsten, 86—is that of the next higher inert gas.

The abnormal behaviour of these complex cyanides on oxidation with acid permanganate has been the subject of much theoretical speculation. Unlike the majority of compounds containing molybdenum and tungsten, which on oxidation with acid permanganate are converted into the sexavalent condition, these complex cyanides pass only to the quinquevalent state. In order to dispel any doubt as to the correctness of formulating the complex tungsten cyanide, $K_4W(CN)_8$, as a derivative of quadrivalent tungsten, Olsson (*Ber.*, 1914, **47**, 917; *Z. anorg. Chem.*, 1914, **88**, 49) showed that on complete oxidation with ammoniacal silver salt solution, two atoms of silver separated for each molecule of the salt oxidised. Further convincing proof of the extent of oxidation by acid permanganate was the isolation of compounds of the type $R_3W(CN)_8$ from the oxidised solution of $K_4W(CN)_8$. Olsson was unsuccessful, however, in isolating the corresponding molybdenum type, $R_3Mo(CN)_8$. By taking special precautions, this has now been done, and not only have salts of this series been prepared, but also the complex *acid* $H_3Mo(CN)_8,3H_2O$ has been isolated. It is also hoped to show that a satisfactory explanation of the abnormal oxidation by acid permanganate is forthcoming from a consideration of the electronic theory of valency.

In researches on the complex cyanides of the type $R_4Mo(CN)_8$, Rosenheim and his co-workers (*Z. anorg. Chem.*, 1909, **65**, 166; 1907, **54**, 97) prepared derivatives where R was replaced by equivalent proportions of cadmium, thallium (univalent), manganese, pyridinium, and the ammines of silver, copper, and nickel. The methods of preparation and the compositions of the silver, copper, thallous, and ammino-silver compounds have been re-examined, confirming Rosenheim's data, whilst the isolation of the new insoluble, dark green *ammino-copper* salt, $[Cu(NH_3)_3]_2Mo(CN)_8$, and the dark blue, soluble *complex salt*, $[Cu\ en_2]_2Mo(CN)_8$, affords interesting examples of copper exhibiting co-ordination numbers of 3 and 4. In addition, a study of the so-called red and blue cyanides of quadrivalent molybdenum has been made, and a bright brick-red, insoluble compound, which is probably the complex acid $H[MoO_2(CN)_2,2H_2O]$, has been prepared by the action of concentrated nitric acid on $K_4Mo(CN)_8$.

Experimental.

Salts of the Type $R_4[Mo(CN)_8]$.—From the reaction of potassium cyanide with the complex chloride of tervalent molybdenum, K_3MoCl_6, Chilesotti (*Gazzetta*, 1904, **34**, ii, 493) obtained a yellow, crystalline salt of the composition $K_4Mo(CN)_8,2H_2O$, in which he assumed that the molybdenum was quadrivalent. The same

compound was isolated later by Rosenheim and Koss (*Z. anorg. Chem.*, 1906, **49**, 148) from the interaction of a derivative of quinquevalent molybdenum, $(NH_4)_2[MoOCl_5]$ or $Mo(OH)_2(CNS)_3(C_5H_5N)_2$, and potassium cyanide. Conductivity data (*ibid.*, 1907, **54**, 97) established that the ionisation was in accordance with the formula $K_4[Mo(CN)_8]$, whilst Collenberg (*ibid.*, 1922, **121**, 298) has confirmed Olsson's results, which indicated the quadrivalency of the central atom.

Tetrapotassium Molybdenum Octacyanide.—The method of Chilesotti (*loc. cit.*) was used. One part by weight of K_3MoCl_6 and 2 parts of potassium cyanide were intimately mixed and 6 parts of water added in small portions, during about 2 hours. The solution was raised to boiling point and concentrated on a water-bath, whereby yellow crystals were obtained. These were separated from the mother-liquor and extracted with small quantities of hot water, and the solution was filtered and allowed to crystallise. Further purification was obtained by redissolution in a little water and precipitation by alcohol with rapid stirring. The small, golden-yellow crystals thus prepared were very pure.

Analysis. It was found necessary to destroy the complex anion completely before the molybdenum could be precipitated quantitatively. The general method used was to digest the compound with boiling concentrated sulphuric acid for some time, dilute the mixture, make it alkaline with ammonia, and then add colourless ammonium sulphide solution and acid as previously described (J., 1924, **125**, 1911). Unfortunately, large quantities of ammonium sulphate have to be eliminated in the potassium estimation [Found : Mo, 19·2; K, 31·2; C, 19·3; N, 22·8. Calc. for $K_4Mo(CN)_8,2H_2O$: Mo, 19·4; K, 31·5; C, 19·4; N, 22·6%].

The compound, which is readily soluble in water, producing a yellow, slightly alkaline solution, is decomposed neither by dilute acids nor by alkalis. Concentrated sulphuric acid is required to effect complete decomposition. It is light-sensitive (Collenberg, *Z. anorg. Chem.*, 1924, **136**, 245), but not to such an extent as the analogous compound of quinquevalent molybdenum. A detailed account of its properties is given by Chilesotti (*loc. cit.*).

Tetrasilver Molybdenum Octacyanide.—Silver nitrate solution was added to a solution of $K_4Mo(CN)_8$, and the yellow silver salt which separated was washed with water and dried in a vacuum desiccator [Found : Ag, 58·3; Mo, 12·9. Calc. for $Ag_4Mo(CN)_8$: Ag, 58·7; Mo, 13·0%]. On being warmed with ammonia (*d* 0·88), this silver salt dissolved, and concentration of the solution over sulphuric acid yielded a yellow, crystalline compound insoluble in water. This was kept over concentrated sulphuric acid until free from the

of ammonia [Found: Ag, 54·5; Mo, 12·1; NH_3, 6·3. Calc. for $Ag_4(NH_3)_3Mo(CN)_8$: Ag, 54·8; Mo, 12·2; NH_3, 6·4%].

Tetrathallous Molybdenum Octacyanide.—This salt was prepared by adding the theoretical amount of a solution of thallous nitrate to a concentrated solution of $K_4Mo(CN)_8$, evaporating the mixture to small bulk, filtering, and allowing the salt to crystallise. The orange-yellow crystals obtained were washed with water and dried on a filter-paper.

Analysis. The substance was boiled with concentrated sulphuric acid until the solution was nearly colourless. On diluting it, making it alkaline with ammonia, and adding colourless ammonium sulphide solution, thallous sulphide was precipitated, which was washed with ammonium sulphide solution and filtered off. Molybdenum was estimated in the usual way in the filtrate and washings. The thallous sulphide was dissolved in dilute nitric acid, the solution evaporated to dryness, and potassium iodide added to an aqueous solution of the residue, precipitating thallous iodide, which was washed by decantation with potassium iodide solution, collected, and treated with alcohol to remove any potassium iodide [Found: Tl, 72·3; Mo, 8·6. Calc. for $Tl_4Mo(CN)_8$: Tl, 72·8; Mo, 8·5%].

The compositions of this salt and of the corresponding silver salt indicate that water of crystallisation, which is present in many of these complex cyanides, is not an essential constituent of the co-ordination complex.

Dicupric Molybdenum Octacyanide.—This was prepared by double decomposition of the potassium complex cyanide with copper sulphate solution. The precipitate was coagulated by boiling, washed with water, and dried in a vacuum desiccator; it was then dark purple.

Analysis. The substance was heated with concentrated sulphuric acid until a nearly colourless solution resulted; this was diluted and made just alkaline with sodium hydroxide, excess of sodium sulphide solution added, and the whole boiled for a few minutes to ensure all the molybdenum being present as the soluble thiomolybdate. The precipitated copper sulphide was filtered off, washed with sodium sulphide solution, then with hydrogen sulphide water, dried, and gently ignited. The residue, after being moistened with pure nitric acid and reheated, was weighed as copper oxide. The molybdenum in the filtrate and washings was precipitated as sulphide by the addition of dilute sulphuric acid, filtered off, and ignited to trioxide [Found: Mo, 22·1; Cu, 29·7. Calc. for $Cu_2Mo(CN)_8$: Mo, 22·3; Cu, 29·5%].

Hexamminodicupric Molybdenum Octacyanide.—By treatment of

the above copper salt with concentrated ammonia solution, Rosenheim (*Z. anorg. Chem.*, 1907, **54**, 97) obtained a dark green ammino-compound to which he assigned the formula $Cu_2(NH_3)_4Mo(CN)_8,7H_2O$. By the use of a similar method, a new *ammino-copper* derivative has been obtained. On addition of ammonia (*d* 0·88) to the purple $Cu_2Mo(CN)_8$, the colour changed to bright green. On warming, the solid dissolved, producing a dark green solution from which, after filtration and standing over sulphuric acid, dark green crystals separated, which were insoluble in water but could be recrystallised from ammonia solution (*ca.* 10*N*). The substance was washed with water and dried in a vacuum over sulphuric acid, whereupon the colour became a lighter green {Found: Mo, 17·8; Cu, 24·1; NH_3, 19·4. $[Cu(NH_3)_3]_2Mo(CN)_8$ requires Mo, 18·0; Cu, 23·9; NH_3, 19·1%}. Treatment with acid removes the ammonia and precipitates the purple $Cu_2Mo(CN)_8$.

Tetraethylenediaminodicupric Molybdenum Octacyanide.—The purple $Cu_2Mo(CN)_8$ (1 mol.) was mixed with ethylenediamine hydrate (4 mols.) and well shaken. A blue substance formed immediately and was recrystallised from water, in which it gave a deep bluish-purple solution. After being dried over sulphuric acid, the new salt was deep blue, readily soluble in warm water, and easily decomposed by dilute acids, $Cu_2Mo(CN)_8$ being precipitated {Found: Cu, 18·8; Mo, 14·3; N, 33·5. $[Cu(en)_2]_2Mo(CN)_8$ requires Cu, 19·0; Mo, 14·3; N, 33·4%}.

Conductivity measurements at 25° indicated, as would be expected from the formula, a maximum of 3 ions in very dilute solutions.

Dilution (litres per mol.)	155	310	620	1240
μ	78·5	104·3	134·4	166·2

For comparison, the values of the molecular conductivities of typical salts at 25° are given:

Dilution (litres per mol.)	128	256	512	1024
NaCl	113	115	117	118
K_2SO_4	246	257	265	273

In the more concentrated solutions, the molecular conductivity is even less than that required for a typical binary electrolyte, but at higher dilutions, although less than that demanded by a ternary electrolyte, it exceeds that of the binary electrolyte.

In the complex kations containing copper, it is possible to assign to the copper co-ordination numbers of 2, 3, and 4, but with the silver salt $[Ag_4(NH_3)_3]Mo(CN)_8$ it is difficult to discern any satisfactory co-ordination number for the silver atom.

Salts of the Type $R_3Mo(CN)_8$.—In attempting to isolate salts of this type, Olsson (*Ber.*, 1914, **47**, 917) added silver nitrate solution

to a solution of $K_4Mo(CN)_8$ which had been as fully oxidised as possible with acid permanganate. Thereby he obtained a reddish-brown precipitate obviously different from the yellow $Ag_4Mo(CN)_8$. By decomposition with potassium chloride solution, this reddish-brown silver salt gave a yellow liquid which could no longer be oxidised by permanganate. From this solution, green crystals of a copper salt were obtained, again distinct from the purple $Cu_2Mo(CN)_8$. The yellow liquid readily decomposed on warming or on exposure to light, yielding molybdic acid, hydrocyanic acid, and $K_4Mo(CN)_8$, and probably contained the salt $K_3Mo(CN)_8$. It appeared that this potassium salt could be satisfactorily isolated only in the absence of light.

Trisilver Molybdenum Octacyanide.—A solution of $K_4Mo(CN)_8$ was oxidised with acid permanganate until a faint pink colour remained. Excess of silver nitrate was then added, the resulting reddish-brown precipitate was washed repeatedly by decantation with water, and then dried in a vacuum. This substance was contaminated with manganese dioxide from the decomposition of the permanganate in the presence of the silver ions; by working with dilute solutions of both $K_4Mo(CN)_8$ and permanganate, however, the amount of dioxide produced was small. The reddish-brown precipitate was triturated with a little potassium chloride solution (insufficient for complete decomposition), and the yellow solution was filtered and again treated with silver nitrate solution. Any slight amount of chloride in the yellow solution is precipitated by the silver nitrate before the reddish-brown silver complex cyanide. Therefore, silver nitrate solution was carefully added until a faint brown precipitate was obtained, the solution again filtered, and the pure reddish-brown salt obtained by the addition of excess silver nitrate solution to the filtrate. The compound was washed with cold water and dried in a vacuum over phosphoric oxide.

Analysis. The silver was estimated as chloride by boiling the compound with concentrated sulphuric acid, diluting the solution, and adding either dilute hydrochloric acid or potassium chloride solution. The molybdenum was estimated in the usual way [Found: Ag, 51·3; Mo, 15·2; N, 17·6. $Ag_3Mo(CN)_8$ requires Ag, 51·6; Mo, 15·2; N, 17·7%].

Tripotassium Molybdenum Octacyanide. — The silver salt, $Ag_3Mo(CN)_8$, was triturated with insufficient potassium chloride solution for complete decomposition. The filtered yellow solution, which contained no chloride, was concentrated in a vacuum desiccator over phosphoric oxide, whereupon yellow needles were obtained. These operations were carried out in a dark room with a

red light, and the solid was preserved in a desiccator covered with black paper. In daylight, the yellow crystals turned reddish-brown [Found: Mo, 22·4; N, 26·4; K, 28·2. $K_3Mo(CN)_8$ requires Mo, 22·8; N, 26·6; K, 27·8%]. Because of its sensitivity to light, conductivity measurements were not carried out on the new complex cyanide. By addition of copper sulphate solution to the yellow solution of the new salt, a grass-green precipitate was obtained, which, after a few minutes' exposure to light, turned purple.

Trihydrogen Molybdenum Octacyanide.—The yellow solution, produced by triturating the complex silver salt with a little dilute hydrochloric acid and filtering, was saturated with hydrogen chloride at the temperature of an ice–salt mixture. A reddish-orange substance separated, which was possibly an addition compound of hydrogen chloride with the required complex acid. This was filtered off and dried in a vacuum over potassium hydroxide and phosphoric oxide, and thereby became orange-coloured and free from hydrogen chloride. The new solid gave a yellow, aqueous solution, from which silver and copper salts precipitated the characteristically coloured complex cyanides of quinquevalent molybdenum. The same compound is obtained if the yellow solution is concentrated in a vacuum over potassium hydroxide and phosphoric oxide, without saturation with hydrogen chloride. In either case, all operations must be conducted in the absence of light. The new *acid* is extremely deliquescent [Found: Mo, 26·7; N, 31·1. $H_3Mo(CN)_8,3H_2O$ requires Mo, 26·6; N, 31·0%].

In order to confirm the constitution of the substance and to demonstrate its freedom from hydrogen chloride, a solution of the complex acid was treated with silver nitrate solution, all the molybdenum being thereby precipitated as $Ag_3Mo(CN)_8$. This precipitate was washed free from silver nitrate, and excess of potassium chloride solution added. The $Ag_3Mo(CN)_8$ was thereby converted quantitatively into silver chloride, which was washed and weighed. Any hydrogen chloride in the original substance would also have been precipitated as silver chloride. 0·2164 G. of the new acid, containing 26·7% of Mo, gave 0·2606 g. of AgCl; hence Mo : AgCl = 1 : 3·02, proving also the absence of hydrogen chloride from the complex acid.

The Abnormal Oxidation of the Complex Cyanides.

On the basis of the electronic theory of valency, an explanation is now available of the abnormal behaviour of the complex cyanides of molybdenum on oxidation with acid permanganate. Estimation of the valency of the molybdenum in $K_4Mo(CN)_8$ through titration with acid permanganate involves the consumption of only one equi-

valent of oxygen for each molecule of salt oxidised, from which one would conclude that the molybdenum was quinquevalent, since the usual end-product would be expected to contain sexavalent molybdenum. This, however, does not agree with the formula of the compound, in which the molybdenum must be quadrivalent. That, by complete oxidation with acid permanganate, the molybdenum in $K_4Mo(CN)_8$ is oxidised from the quadrivalent to the quinquevalent condition, is now clearly shown by the isolation of the complex salts $R_3Mo(CN)_8$ from the fully oxidised solution of $K_4Mo(CN)_8$. Ephraim ("Inorganic Chemistry," English transl., 1926, p. 280), commenting on this exceptional oxidation, says: "It is not easy to see the explanation of this anomaly, but it is possible that the metal atom is surrounded by voluminous radicles which are fairly firmly attached." A much more satisfactory explanation is forthcoming from a consideration of the effective atomic number of the central atom in the various complex salts involved in the preparation of the complex cyanides. The salt $K_4Mo(CN)_8$ is normally prepared by the interaction of potassium cyanide with complex compounds of either tervalent or quinquevalent molybdenum. In the former case the reaction may be conveniently formulated as $K_3MoCl_6 + 8KCN + \frac{1}{2}H_2O + \frac{1}{2}O(air) = K_4Mo(CN)_8 + 6KCl + KOH$. The instability of the intermediate $K_3Mo(CN)_6$—a salt as yet unisolated—which reverts to the stable $K_4Mo(CN)_8$, can be readily appreciated when it is seen that the effective atomic number of the molybdenum is only 51, whereas in the stable compound it is 54. In the preparation from the complex chlorides of quinquevalent molybdenum, R_2MoOCl_5, the importance of the effective atomic number of the molybdenum in $K_4Mo(CN)_8$ is again emphasised. The reaction may be considered as occurring in the following stages:

$$K_2MoOCl_5 + 5KCN = K_2MoO(CN)_5 + 5KCl$$
$$K_2MoO(CN)_5 + 3KCN + H_2O = K_3Mo(CN)_8 + 2KOH$$
$$2K_3Mo(CN)_8 + 2KOH = 2K_4Mo(CN)_8 + H_2O + \tfrac{1}{2}O_2$$

[compare $2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + \frac{1}{2}O_2$]

The instability of the salt $K_2MoO(CN)_5$ follows as a consequence of the low effective atomic number, *viz.*, 49, of the molybdenum atom, whilst the formation of $K_4Mo(CN)_8$ from $K_3Mo(CN)_8$ involves a change of an effective atomic number of 53 to 54—a clear proof of the influence of an inert-gas structure in determining chemical stability. The inability to oxidise $K_4Mo(CN)_8$ to the salt $K_2Mo(CN)_8$ of sexavalent molybdenum, with an effective atomic number of 52, is not surprising in view of the experimental evidence that $K_3Mo(CN)_8$ functions as an oxidising agent in order to revert to

the more stable $K_4Mo(CN)_8$. This change, as has been previously mentioned, is readily brought about by light or by the action of heat. Further evidence of the instability of the system $[Mo(CN)_8]'''$ is seen in the rapidity with which, in light, the green complex salt $Cu_3[Mo(CN)_8]_2$ reverts to the purple $Cu_2[Mo(CN)_8]$. Oxidation to the sexavalent condition is realised only by complete decomposition of the complex anion. When the complex salt $K_4Mo(CN)_8$ is oxidised by ammoniacal silver nitrate, the molybdenum is converted into the trioxide.

The Red and the Blue Cyanides of Quadrivalent Molybdenum.

Just as the yellow cyanide, $K_4Mo(CN)_8$, results from the reaction of potassium cyanide with salts of tervalent and quinquevalent molybdenum, so by adjusting the proportion of the reactants so that 1 g.-mol. of the salt of quinquevalent molybdenum reacts with 4 g.-mols. of potassium cyanide, a red cyanide is obtained, which may be formulated as either $[Mo(OH)_4(CN)_4]K_4,xH_2O$ or $[MoO_2(CN)_4]K_4,(x + 2)H_2O$. Moreover, by use of excess potassium cyanide the red will revert to the yellow salt in accordance with the equations

$$[Mo(OH)_4(CN)_4]R_4 + 4RCN = [Mo(CN)_8]R_4 + 4ROH,$$
$$[MoO_2(CN)_4]R_4 + 4RCN = [Mo(CN)_8]R_4 + 2R_2O.$$

By strong dehydration over sulphuric acid, or by cautious heating, these red cyanides become blue; their aqueous solutions also are blue. Addition of potassium hydroxide in sufficient concentration to the blue aqueous solution results in the reprecipitation of the red cyanide. The addition of alcohol to the blue aqueous solution causes the precipitation of a blue solid, which, after being dissolved in water and reprecipitated several times, has a composition for which various formulæ have been proposed. Two in particular may be noted: $MoO_2,4KCN,5H_2O$ and $Mo(OH)_2(CN)_2,3KCN$. These show the quadrivalency of the molybdenum, but indicate the possibility that quite different blue complex cyanides exist. With the object of investigating the reasons for these striking colour changes, samples of the red and the blue cyanides were prepared and examined.

The Red Cyanides.—By the reduction of an acid solution of molybdenum trioxide with potassium iodide, removal of the excess iodine, and subsequent treatment with potassium cyanide and hydroxide, Heide and Hofmann (*Z. anorg. Chem.*, 1896, **12**, 277) obtained red crystals to which they assigned the formula

$$4KCN,MoO_2,10H_2O.$$

Rosenheim, Garfunkel, and Kohn (*ibid.*, 1910, **65**, 166) obtained a similar compound by treating $(NH_4)_2MoOCl_5$ or

$$Mo(OH)_2(CNS)_3(C_5H_5N)_2$$

—salts of quinquevalent molybdenum—with potassium cyanide, and subsequently adding potassium hydroxide. The method used by the present authors followed that of Péchard (*Compt. rend.*, 1894, **118**, 804), who dissolved molybdenum pentoxide in potassium cyanide solution, and precipitated the red crystals by the addition of solid potassium hydroxide to the blue solution.

300 C.c. of a solution of molybdenum trioxide (10%) in hydrochloric acid (3*N*) were electrolysed in a diaphragm cell for 2 hours (1 amp.; 8 volts) and concentrated at *ca.* 70° to a very small bulk. On careful addition of very concentrated potassium hydroxide solution, the brown hydroxide of quinquevalent molybdenum was obtained. On addition of the theoretical amount of potassium cyanide (54 g.) as a saturated solution, the hydroxide slowly dissolved, producing a blue solution, which was filtered and concentrated under diminished pressure at *ca.* 70° to a small bulk (30—40 c.c.). Red crystals were deposited on addition of solid potassium hydroxide to this blue solution. By means of a little water and then alcohol, the crystals were freed from potassium hydroxide. They are stable towards dilute mineral acids, but appear to be decomposed by organic acids, such as salicylic or oxalic acid, although no definite compounds could be obtained. In the presence of concentrated potassium hydroxide, the crystals exhibit a bright red colour, but as the hydroxide is removed the colour becomes bluish-red.

Analysis. An aqueous solution of the substance was oxidised with hydrogen peroxide and made alkaline with ammonia, and colourless ammonium sulphide was added. Addition of dilute sulphuric acid precipitated the molybdenum as sulphide, which was ignited and weighed as trioxide. The potassium in the filtrate was weighed as sulphate {Found : Mo, 19·3; K, 31·1; C, 9·9; H, 2·4; N, 11·5. Calc. for $K_4[Mo(OH)_4(CN)_4],4H_2O$: Mo, 19·3; K, 31·4; C, 9·6; H, 2·4; N, 11·3%}.

Even when the crystals did not contain any free potassium hydroxide, their aqueous solution gave an alkaline reaction with phenolphthalein, suggesting hydrolysis. This view is supported by the conductivity data, which indicate that, even at 1°, more than 5 ions are present in dilute solutions. The table gives the value of μ for various dilutions v (as litres per mol.).

v	23·5	47	94	188
μ	275·6	298·4	320·6	342·3

(compare this vol., p. 516, Table IV, for conductivities of typical salts at 1°).

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

G. of substance per 100 g. water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
0·7136	0·01440	5·16	96·2
1·517	0·03560	5·06	97·9
2·636	0·05314	4·85	102·6

These results indicate the correctness of a formulation which requires 5 ions, but they also show that slow hydrolysis takes place in dilute aqueous solution.

The Blue Cyanides.—An aqueous solution of the red cyanide was treated with alcohol, whereby a blue precipitate resulted. The mother-liquor was alkaline to phenolphthalein, indicating that by the conversion of the red into the blue cyanide, potassium hydroxide was removed. The blue solid was redissolved in water and re-precipitated with alcohol; these operations were repeated until the mother-liquor from the precipitation was no longer alkaline. Thereby a blue substance was obtained {Found: Mo, 22·5; K, 28·0; C, 11·5; N, 13·1. $K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O$ requires Mo, 22·7; K, 27·8; C, 11·3; N, 13·3%}.

The aqueous solution of this compound was alkaline to phenolphthalein, and with potassium cyanide yielded the yellow $K_4Mo(CN)_8$. The blue substance was prepared several times by the above method and always had the same composition. The formulation given above was in accordance with the results of molecular-weight and conductivity determinations, which indicated that 4 ions were present in solution but that gradual hydrolysis also took place.

Molecular-weight Determinations.

G. of substance per 100 g. water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
0·6618	0·01554	4·25	99·3
1·235	0·02898	4·23	99·7

Molecular-conductivity Determinations, at 1°.

v	35·5	71	142	284
μ	198·8	215·5	232·8	250·0

The Relationship of the Red and the Blue Cyanides.—The fact that the red cyanide becomes blue on dehydration and yet yields a blue aqueous solution seems to depend on the equilibrium

$$K_4[Mo(OH)_4(CN)_4],4H_2O \rightleftharpoons K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O + KOH + H_2O.$$

It was noticed that the red colour of the complex cyanide is attained only in the presence of concentrated potassium hydroxide, and that on removal of this free alkali the pure complex salt becomes bluish-violet. It appears probable, therefore, that on dehydration and on dissolution in water, a decomposition takes place in accordance with the above equation. A co-ordination number of 8 is

the molybdenum atom in the red cyanides seems indicated by the fact that on cautious dehydration over sulphuric acid or at 100° they retain 2 mols. of the associated water, suggesting the formula $R_4[MoO_2(CN)_4,2H_2O]aq.$ or $R_4[Mo(OH)_4(CN)_4]aq.$

Brick-red, Insoluble Molybdenum Cyanide.—Chilesotti (*Gazzetta*, 1904, **34**, ii, 493) noticed that the oxidation of the yellow quadrivalent cyanide by means of concentrated nitric acid resulted in the separation of a brick-red, insoluble compound, which he did not further examine.

When $K_4Mo(CN)_8$ was heated with even dilute nitric acid (*ca.* 6*N*) in a test-tube, this compound was obtained pure, but when the experiment was made in an open dish, varying amounts of molybdic acid were formed. The brick-red compound was washed with cold water, in which it was but slightly soluble, and dried in a desiccator over sulphuric acid.

Analysis. The substance was heated with pure sulphuric acid until the solution was colourless, and the molybdenum precipitated as previously described {Found: Mo, 43·8; N, 12·8; C, 11·0; H, 1·8. $H[MoO_2(CN)_2,2H_2O]$ requires Mo, 44·2; N, 12·9; C, 11·0; H, 2·3%}.

Valency. A solution of the substance in dilute aqueous ammonia was made acid with sulphuric acid and titrated with permanganate. On the assumption that the molybdenum in the compound has a valency of 5, the theoretical content of molybdenum calculated from the titration is 44·8%. By gravimetric means it was found to be 43·8%. Hence the molybdenum is quinquevalent.

The solid is soluble in hot water, giving a yellow solution. It is much more readily soluble in ammonia or alkalis, suggesting an acidic structure. In view of this, it is probably correctly formulated as above.

This new derivative is of interest as indicating that on oxidation the quinquevalent molybdenum still persists as a complex anion, but that on oxidation to the sexavalent state complete disruption of the complex ion takes place, a fact which is in complete agreement with the theoretical considerations previously advanced to explain the abnormal oxidation of the yellow complex cyanides.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCCXCVIII.—*Equilibrium Diagram of the System Thallium–Phosphorus.*

By Qasim Ali Mansuri.

The system thallium–phosphorus has not hitherto been investigated. Thallium was prepared as previously described by the author (*J. Inst. Metals*, 1922, **28**, 453); its purity was 99·5%, the chief impurity being iron (less than 0·3%). Merck's pure red phosphorus was repeatedly boiled with water and then showed a content of 99·91%.

Preparation of Alloys.—Molten thallium alloyed readily with phosphorus, and the action was more marked above 400°. When more than 2·5% of phosphorus had been added, the alloys separated into two layers, the upper one being dark and brittle, and the lower layer soft. The dark substance was readily oxidised to phosphoric acid on being exposed to the air.

Thermal Analysis.—To avoid oxidation of the mixtures, they were prepared in hard-glass tubes from weighed quantities of thallium or the alloy and not more than 1 g. of free phosphorus at a time. The tubes were then evacuated and sealed and the cooling curves were obtained by applying the hot junction of a nichrome–constantan couple to the outside of the tube, contact being made more intimate by means of fireclay. The tubes were packed in sand in an iron tube about 1½ inches in diameter and 1 foot in length, the whole being heated in an electrical tube furnace. The molten alloy was thoroughly mixed by repeatedly tilting the furnace, and the cooling curves were then taken.

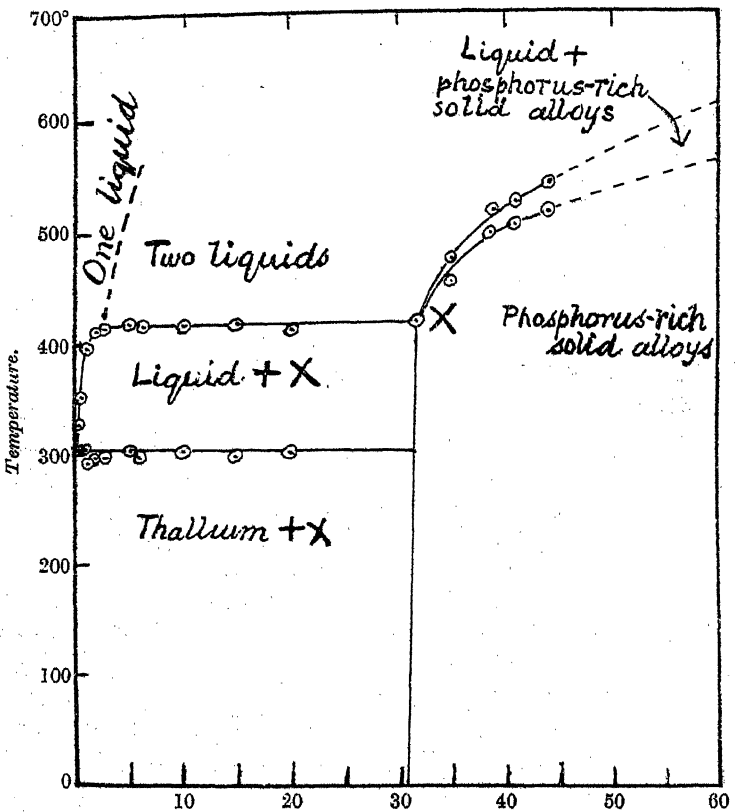
A suspended mirror galvanometer and scale were used for taking temperatures, the rate of cooling being about 8° per minute at high temperatures and about 5° per minute below 300°. Half-minute readings gave the following thermal arrests from which the equilibrium diagram was constructed.

Alloy No.	P, % by weight.	Thermal arrests. 1.	2.	Alloy No.	P, % by weight.	Thermal arrests. 1.	2.
1	0·00	—	303°	9	10·00	416°	303°
2	0·17	328°	302	10	15·00	418	298
3	0·38	352	303	11	20·00	412	300
4	0·87	396	290	12	31·40	420	—
5	2·00	410	296	13	35·00	476	456
6	2·50	412	296	14	38·75	520	500
7	5·00	418	302	15	41·20	528	506
8	6·08	416	296	16	43·90	546	520

Alloys containing from 2·5% to about 27% of phosphorus show two layers, the lower layer being practically pure thallium, and

freezing at the melting point of that metal. Thallium, therefore, does not seem to dissolve any of the upper layer at its melting point. The upper layer freezes at about 420°. In alloys containing more than 2·5% of phosphorus, the two layers may dissolve in each other at higher temperatures than 420°. An attempt was made to find at what temperatures the two layers dissolved in each other

FIG. 1.



Equilibrium diagram of the system thallium–phosphorus.

by heating the alloys to definite temperatures above 420° and chilling them, but a considerable pressure was developed and the tubes burst. However, an alloy containing about 0·2% of phosphorus was heated to 350° and chilled; although this burst in water, a small piece was obtained which, on being polished, was found to be uniform, showing that in this alloy the two layers were miscible at about 350°. The solubility of the two layers in each other is there-

fore dependent upon the temperature. A short dotted line has been drawn on the left side of the diagram to indicate this solubility.

Composition of the Alloys.—As most of the alloys were not homogeneous, they were not analysed, but their compositions were deduced from the weights of the constituents in the tubes. The upper dark layer, which was brittle, could be separated by powdering; it contained 31·4—31·5% of phosphorus. The lower layer contained no phosphorus. The thallium was estimated as described by the author (*loc. cit.*), and the quantity of phosphorus was found by difference.

Conclusions.

1. Up to 45% of phosphorus, thallium and phosphorus alloy in all proportions.

2. They form a homogeneous substance, X, containing about 31·4% of phosphorus and melting at about 420°. At this temperature, about 8% of this substance dissolves in thallium, to give an alloy containing 2·5% of phosphorus. Owing to the low solubility of X in thallium, the alloys separate into two layers, the upper layer being X and the lower layer a solution of a small quantity of X in thallium. On cooling, thallium gradually loses all the X dissolved in it and freezes at its melting point.

3. Quantities of phosphorus in excess of 31·4% dissolve in X and form solid solutions, which freeze at temperatures above 420° and over a temperature range. The phosphorus may exist as yellow phosphorus in these alloys, for they take fire when rubbed on emery paper.

4. The substance X tends to dissociate into its constituents at all temperatures, and a high pressure is therefore necessary for its formation; owing to this high pressure, the solubility curve of X in thallium could not be studied.

ALIGARH MUSLIM UNIVERSITY,
ALIGARH, INDIA.

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CCCXCIX.—*An Auto-poisoning Phenomenon shown by Catalytically Active Copper at Moderate Temperatures.*

By FREDERICK HURN CONSTABLE.

THE author has previously shown (this vol., p. 1578) the extent to which sintering by heat treatment reduces the surface area and catalytic activity of copper, and has also provided definite evidence that the " centres of activity " collapse when the kinetic energy of the constituent atoms becomes sufficient. The heterogeneous nature

of the active surface is now well recognised, and the present paper shows how the active centres may be rendered inactive during the catalysis of a chemical change, even when precautions are taken that the reactant is quite pure, and that the temperatures are below those at which sintering of the centres occurs in a vacuum, in spite of the fact that the reaction proceeds with the absorption of heat.

When a copper catalyst is used to dehydrogenate alcoholic substances at temperatures above 280°, it is found that the activity decays with time. Measurements have been made on the variation of activity with time, and on the effect of temperature on the rate of decay. The catalyst is stable when heated alone to the temperature used, so the poisoning is due to the interaction of the copper and the alcohol. It has been shown that the method of preparation of the catalyst does not alter the temperature at which the effect becomes noticeable, though it seems to have a considerable influence on the rate of poisoning, the rate of decay of the preparation from copper oxalate being about 5 times greater than that of copper reduced from oxide at the same temperature (*Proc. Roy. Soc.*, 1926, *A*, **110**, 297, Fig. 2, curve 5, and Fig. 5).

Experimental.

The ethyl alcohol was twice refluxed with lime, distilled through a Dufton column, and collected in a receiver fitted with a phosphorus pentoxide guard tube; it had b. p. 78·30° ± 0·01°/760 mm. The apparatus used has already been described (*Proc. Camb. Phil. Soc.*, 1925, **22**, 739). The initial stages of the reaction were always studied, and the rate of flow of the alcohol was regulated so that the concentration of the aldehyde over the catalyst was never greater than 1%. The amount of copper used as a catalyst had to be decreased as the temperature of experiment was increased. The rate of poisoning at constant temperature is not dependent on the rate of passage of the alcohol vapour when this exceeds a definite limiting value, and is therefore not dependent on the small concentration of the aldehyde in the vapour above the catalyst.

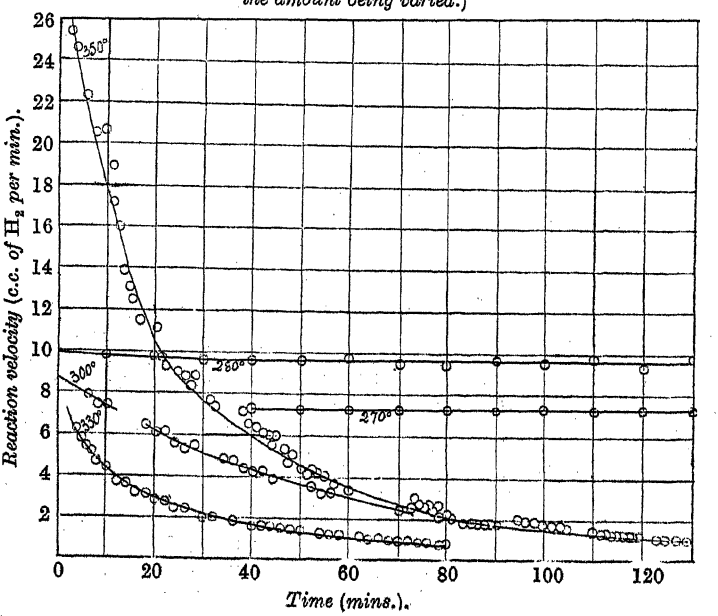
The reaction tube was filled with carbon monoxide at the constant temperature at which the decay of activity was to be measured, and the copper oxide thereby reduced. Blank experiments were made with water vapour instead of alcohol in order to determine the magnitude of the correction which had to be applied on account of the displacement of carbon monoxide from the reaction tube in the initial stages of the reaction. The correction was very large in the first few minutes after the bulk of the gas had suddenly been displaced by the admission of the vapour stream. It was found that a current of steam produced by the vaporisation of 1·28 c.c. of water

per minute would take about 10 seconds to pass the glass valve B_2 (*Proc. Camb. Phil. Soc., loc. cit.*, Fig. 1), and during this time the valve condensed the gas stream and was being warmed; then followed a very rapid evolution of gas from the reaction tube, lasting about 25 seconds, which stopped suddenly when the vapour stream reached the condenser K. The gas which had escaped removal by diffusion was then evolved at a continually decreasing rate, which was carefully measured; the readings so obtained are in Table I,

FIG. 1.

Decay curves at 270—350°.

(*The catalyst was produced by reduction at the temperature of experiment, the amount being varied.*)



the time from the commencement being given in minutes, and the rate of evolution in c.c. per minute. This correction was applied to

TABLE I.

Time	5	10	15	20	25	30	35
Rate	0·80	0·45	0·33	0·30	0·22	0·20	0·18

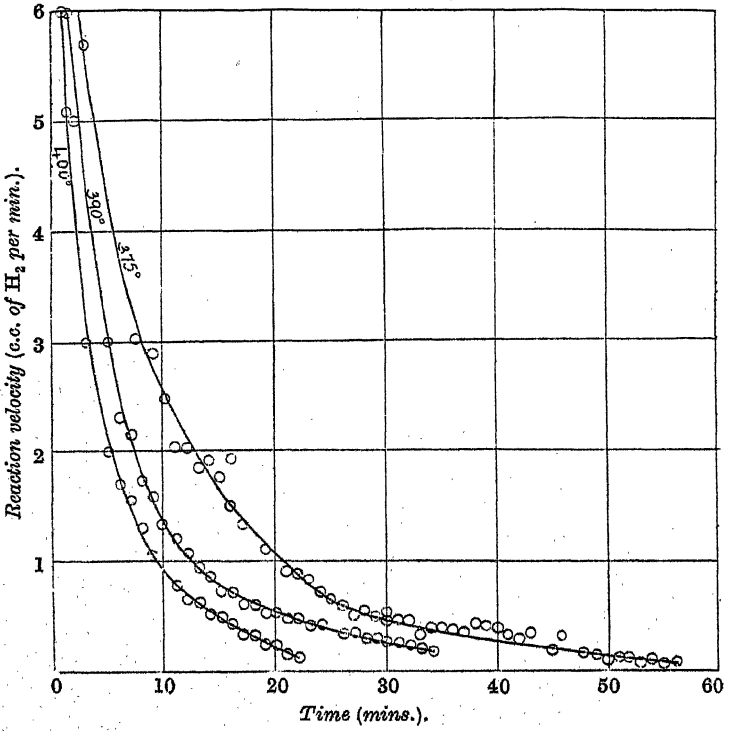
all the measurements made, but owing to variations in this quantity with the rate of flow the magnitude of the correction in the period 0—5 minutes is subject to considerable uncertainty. The measurements are thus somewhat untrustworthy except when the reaction

velocity is large, and if the activity is short-lived the precise form of the curve may be doubtful, *e.g.*, at 400°.

Procedure.—The alcohol stream was turned on, and 20 seconds were allowed for the time taken by the gas stream to reach the copper, and hence for the commencement of the reaction. The gas burette T was read every 30 seconds in the first 5 minutes, and then every minute until the activity became inappreciable. The corrected

FIG. 2.

Decay curves at 375—400°.



results of the experiments are shown in Figs. 1 and 2, and the fractional reaction velocities during each decay are given with the corresponding temperatures in Fig. 3. The value of the initial activity was obtained by extrapolation of the measurements in the very early stages of the poisoning.

Examination shows that the data follow neither a simple logarithmic law nor a reciprocal law. The initial logarithmic rate of decay, $d \log v/dt = 1/v \,.\, (dv/dt)$, is considerably retarded as the time proceeds. One typical set of observations at 350° is given in Table II,

TABLE II.

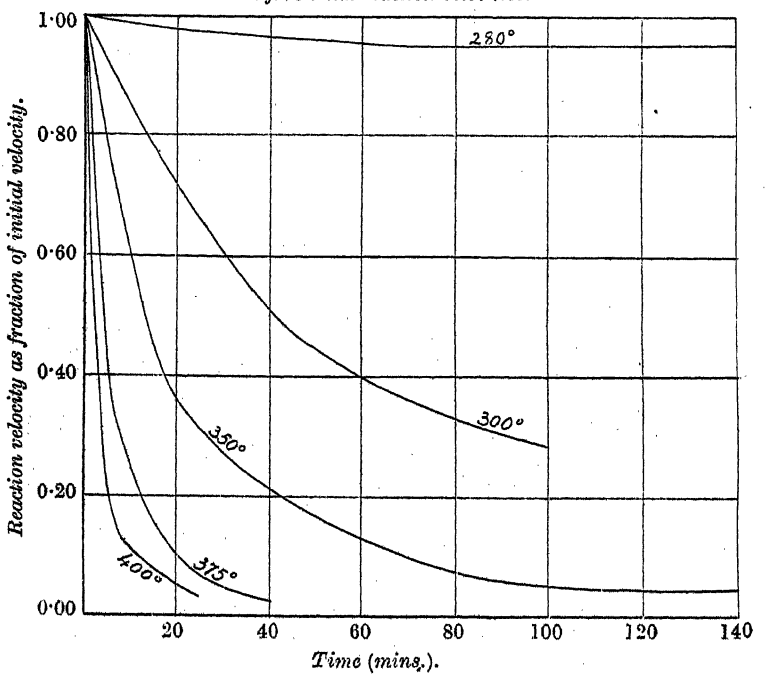
Time	0	10	20	30	40	50	60
Velocity	29·0	18·0	10·7	8·3	6·6	4·8	3·6
Time	70	80	90	100	110	120	130
Velocity	2·7	2·0	1·8	1·5	1·3	1·1	1·0

the time being in minutes, and the reaction velocity in c.c. of hydrogen (reduced to *N.T.P.*) evolved per minute.

It is thought that these data may represent a particular case of the selective poisoning of a distribution of centres of activity, and the

FIG. 3.

The fractional reaction velocities.



question is still under investigation. In the absence of definite knowledge of the law of decay, the time required for the velocity five minutes after the commencement to fall to one-tenth of its value has been used as a measure of the rate of poisoning at various temperatures; these times (in mins.), as read from the curves, are shown in Table III.

TABLE III.

Variation of Rate of Poisoning with Temperature.

Temp.	280°	300°	330°	350°	375°	390°	400°
Time	Very large	200	90	65	30	25	18

The rate of poisoning increases rapidly with the temperature, and is so fast that it can hardly be observed above 400°.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, November 8th*, 1927.]

CCCC.—*Substitution Products of 3-Nitro- and 3-Amino-diphenyl.*

By WILLIAM BLAKEY and HAROLD ARCHIBALD SCARBOROUGH.

THE study of the orientation of substituents in 2-amino- and in 4-amino-diphenyl and in their acetyl derivatives (J., 1926, 557; this vol., pp. 89, 1133) has now been extended to a consideration of the substitution products of 3-nitro- and of 3-amino-diphenyl. The inclusion of 3-nitrodiphenyl in the scope of the work makes it possible to compare the behaviour of the three possible mononitrodiphenyls as well as the three monoaminodiphenyls.

The chlorination of 3-nitrodiphenyl took place readily in the presence of a powerful catalyst and at moderately high temperatures. The product was a mixture of compounds, containing one to four atoms of chlorine per molecule, the composition of which depended on the temperature and the duration of the chlorination. From these mixtures, 4′-*chloro*-, 2′ : 4′-*dichloro*-, a *tri*- and a *tetrachloro*-3-*nitrodiphenyl* were isolated. Isomeric mono- and dichlorination products could not be isolated from the semi-solid matter deposited on slow evaporation of the crystallising media. A structure has not been assigned to the higher chlorination products, although the evidence indicated that 2′ : 4′ : 5-trichloro- and 2′ : 4′ : 5 : 6′-tetrachloro-3-nitrodiphenyl had been isolated. The possibility that a chlorine atom was substituted in the 2-, 4-, or 6-position seems to be excluded, since piperidine did not react with either of these compounds (compare Le Fèvre and Turner, this vol., p. 1113).

3-Nitrodiphenyl on bromination yielded 4′-*bromo*-3-*nitrodiphenyl* as the sole product. The introduction of a second bromine atom could not be effected under the most drastic conditions.

The nitration of 3-nitrodiphenyl in fuming nitric acid solution yielded a mixture of 3 : 4′- and 2′ : 3-dinitrodiphenyl. Further nitration, in sulphuric acid solution, of each of these isomerides led to the same product; and since this product on treatment with piperidine yielded 2′ : 3 : 4′-trinitro-4-piperidinodiphenyl (Le Fèvre and Turner, J., 1926, 2041), it must have the structure 2′ : 3 : 4 : 4′-*tetranitrodiphenyl*. Attempts were made to prepare a trinitrodi-

phenyl, but the product proved to be a mixture which could not be separated into its constituents.

The direct chlorination of 3-aminodiphenyl in glacial acetic acid and in carbon tetrachloride solution gave black, resinous masses which were not further investigated. 3-Acetamidodiphenyl, however, gave a stable N-*chloroamine* which could be converted, on treatment with alcohol and acetic acid, into 4-chloro-3-acetamidodiphenyl. The same product was obtained by direct chlorination of 3-acetamidodiphenyl in glacial acetic acid solution. An unstable *N*-chloroamine was obtained by treating 4-chloro-3-acetamidodiphenyl with sodium hypochlorite; the evolution of free chlorine from this compound may be taken as an indication that a second chlorine atom cannot be introduced into either nucleus by the indirect method.

Bromination of the free base in carbon tetrachloride solution yielded 4-*bromo*-3-*aminodiphenyl hydrobromide* and after prolonged treatment 2 : 4 : 6-*tribromo*-3-*aminodiphenyl*. In acetic acid solution bromination of the free base gave a quantitative yield of 2 : 4 : 6-*tribromo*-3-*aminodiphenyl*. Under the usual experimental conditions, 3-acetamidodiphenyl did not yield an *N*-bromoamine. Direct bromination of the acetyl derivative in glacial acetic acid solution at the ordinary temperature gave a nearly quantitative yield of 4-*bromo*-3-*acetamidodiphenyl*; in the presence of excess bromine and at 100—120°, 4 : 6-*dibromo*-3-*acetamidodiphenyl* was obtained. Higher bromination products did not appear to be formed.

On nitration of 3-acetamidodiphenyl in a mixture of glacial acetic acid and acetic anhydride at 70°, 4-*nitro*-3-*acetamidodiphenyl* was isolated in an approximately 50% yield; the residue was a viscid oil from which a crystalline compound could not be obtained. Nitration of 3-acetamidodiphenyl and of 4-bromo-3-acetamidodiphenyl in fuming nitric acid solution yielded 4′-*nitro*-3-*acetamidodiphenyl* and 4-*bromo*-4′-*nitro*-3-*acetamidodiphenyl*, respectively.

A comparison of the results obtained on the introduction of a further substituent into the isomeric mononitrodiphenyls shows that there is a great similarity of behaviour. Thus in each case further substitution takes place in the 2′- or the 4′-position of the unsubstituted nucleus. Bromination yields one product only, the bromine atom entering the 4′-position, and further bromination cannot be effected (compare Turner and Le Fèvre, J., 1926, 2041). The nitration of each of the isomerides yields two dinitrodiphenyls, the entering group substituting in the 2′- or the 4′-position. The relative proportion in which these isomerides are formed appears to vary with the position of the nitro-group originally present, since

3-nitrodiphenyl yields a much higher percentage of a product substituted in the 4′-position than does 4-nitrodiphenyl (compare Bell and Kenyon, J., 1926, 2705). The formation of 2′ : 3 : 4 : 4′-*tetranitrodiphenyl*, in almost quantitative yield, by the further nitration of 2′ : 3- and of 3 : 4′-dinitrodiphenyl is of considerable interest, since compounds having this orientation of their substituents may be obtained from widely different starting points; thus 4-bromo-2′-nitro-, 4-bromo-4′-nitro-, and 4 : 4′-dibromo-diphenyl yield products of this type on nitration.

A comparison of the substitution products of the isomeric monoaminodiphenyls shows that bromination can be carried out progressively until each position in the *op*-relationship to the amino-group has been substituted. The *p*-position to the amino-group is not necessarily the first position to be attacked, as will be seen from a comparison of 2- and 3-aminodiphenyl.

The acetyl derivatives of the three bases form stable *N*-chloroamines which may be converted into nuclear-substituted compounds, but in each case one chlorine atom only may be introduced by this method. Direct halogenation of the acetyl derivatives cannot be carried as far as in the case of the free bases, one position in the ring containing the acetamido-group resisting substitution.

The product isolated on nitration of any of the acetyl derivatives in fuming nitric acid solution or in solution in a strong mineral acid is one substituted in the 4′-position, whereas the product isolated on nitration in acetic acid solution is one substituted in the ring containing the acetamido-group.

4-Acetamidodiphenyl appears to differ from its isomerides in that bromination in the 4′-position can take place without previous substitution in the 3-position.

In a previous communication (J., 1926, 557), tentative rules for the orientation of substituents in the diphenyl series were proposed. The increased data now available show that but little modification of those rules is needed. It was assumed that the linkage between the two nuclei of diphenyl was of such a nature that either phenyl group, like all other hydrocarbon residues, acted as a negative (*op*-directive) group. It now seems well established that the directive power of the phenyl group is appreciably less than that due to the acetamido-group, but is greater than that due to chlorine or bromine.

The directive power of the groups C_6H_4X and C_6H_3XY depends on the nature of the substituents X and Y: when X or Y inhibits further substitution in the nucleus in which it occurs, the directive power of the group as a whole will be decreased, and this decrease becomes more marked when X or Y is a positive group.

EXPERIMENTAL.

3-Nitrodiphenyl.—Bamberger's method (*Ber.*, 1896, **29**, 446; see also Jacobsen, *Ber.*, 1903, **36**, 4083; Gomberg, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372), slightly modified, was found to be the most economical for the preparation in bulk. A paste of 50 g. of *m*-nitroaniline and 80 c.c. of concentrated hydrochloric acid was treated with a solution of 35 g. of sodium nitrite in 100 c.c. of water. Frothing was diminished by the addition of thiophen-free benzene, the volume of which was made up to 300 c.c. on completion of the reaction. This mixture was made alkaline with a 15% solution of sodium hydroxide (*ca.* 300 c.c., added drop by drop) and then acidified with glacial acetic acid. The whole series of operations was carried out below 5° and with vigorous stirring. The semi-solid mass was heated on the water-bath for 30 minutes, the sodium acetate removed, and the benzene layer separated from the aqueous layer and treated with benzene–light petroleum (b. p. 40—60°) to precipitate tar. The clear liquid was decanted, concentrated to about one-tenth of its bulk, and treated with light petroleum so long as tar separated. The clear liquid was decanted, washed with dilute sodium hydroxide solution and with water, and dried over fused sodium sulphate. The sodium acetate and the tars were boiled with light petroleum, and the extract was worked up in the same manner as for the main yield. The 3-nitrodiphenyl crystallised from alcohol in pale yellow needles (yield, 10—12 g.), m. p. 62°.

4′-Chloro-3-nitrodiphenyl was prepared by passing dry chlorine into a mixture of 10 g. of 3-nitrodiphenyl and 1 g. of ferric chloride, heated at 80°, until the gain in weight was 2 g.; or by passing chlorine into a 10% solution of 3-nitrodiphenyl in carbon tetrachloride in the presence of a trace of iodine and keeping the solution for several days. The product after repeated crystallisations from methyl alcohol separated in fine, white needles, m. p. 89° (Found: Cl, 14·9. $C_{12}H_8O_2NCl$ requires Cl, 15·2%).

4′-Chloro-3-acetamidodiphenyl.—5 G. of 4′-chloro-3-nitrodiphenyl in 50 c.c. of alcohol were refluxed with 25 g. of stannous chloride in 25 c.c. of concentrated hydrochloric acid for 6 hours and the mixture was then cooled and rendered alkaline with 30% sodium hydroxide solution. The base, isolated by means of ether, was treated with excess of acetyl chloride in pyridine solution. The product crystallised from methyl alcohol in needles, m. p. 184° (Found: Cl, 14·6. $C_{14}H_{12}ONCl$ requires Cl, 14·45%).

By the hydrolysis of the acetyl derivative with alcoholic hydrochloric acid *4′-chloro-3-aminodiphenyl* was obtained. It separated from methyl alcohol in large needles, m. p. 82° (Found: Cl, 17·4.

$C_{12}H_{10}NCl$ requires Cl, 17·45%), and on oxidation with chromic anhydride in glacial acetic acid solution yielded *p*-chlorobenzoic acid (m. p. 240°).

2′ : 4′-*Dichloro*-3-*nitrodiphenyl* was obtained when dry chlorine was led into a mixture of 5 g. of 3-nitrodiphenyl and 1 g. of ferric chloride, heated at 100°, until the gain in weight was 2 g. The product was extracted with methyl alcohol and crystallised repeatedly from this solvent or from dilute acetic acid. It separated in needles, m. p. 115° (yield, 2—3 g.) (Found: Cl, 26·35. $C_{12}H_7O_2NCl_2$ requires Cl, 26·5%).

On reduction of the dichloro-compound with alcoholic stannous chloride solution in the presence of a large amount of concentrated hydrochloric acid, extraction of the free base, and acetylation, 2′ : 4 : 4′-*trichloro*-3-*acetamidodiphenyl* was obtained. It separated from dilute methyl alcohol in needles, m. p. 170° (Found: C, 53·6; H, 3·15. $C_{14}H_{10}ONCl_3$ requires C, 53·4; H, 3·2%).

2′ : 4 : 4′-*Trichloro*-3-*aminodiphenyl* was obtained on hydrolysis of the acetyl derivative. It separated from dilute methyl alcohol in needles, m. p. 105° (Found: Cl, 38·9. $C_{12}H_8NCl_3$ requires Cl, 39·1%).

Oxidation of the base with chromic anhydride in glacial acetic acid solution yielded 2 : 4-dichlorobenzoic acid (m. p. 161°). The introduction of the chlorine atom into the molecule during the reduction of the nitro-compound would lead to a product substituted in the ring containing the amino-group (compare Blanksma, *Rec. trav. chim.*, 1906, **25**, 365; Scarborough and Waters, this vol., p. 89); thus to the nitro-compound may be assigned the structure 2′ : 4′-dichloro-3-nitrodiphenyl.

Trichloro-3-*nitrodiphenyl* was obtained together with mono- and di-chloro-derivatives when chlorine was passed into a mixture of 3-nitrodiphenyl and ferric chloride at 100° for some hours. The product was extracted with acetone and repeatedly crystallised from this solvent or from benzene. It separated in needles, m. p. 211°. The yield was less than 20% of the theoretical (Found: Cl, 35·2. $C_{12}H_6O_2NCl_3$ requires Cl, 35·2%).

Tetrachloro-3-*nitrodiphenyl* was obtained when the chlorination was carried out at 120°. The product was extracted with acetone and recrystallised from this solvent repeatedly. It separated from alcohol as a matted mass of fine needles, m. p. 175° (Found: Cl, 42·5. $C_{12}H_5O_2NCl_4$ requires Cl, 42·2%).

4′-*Bromo*-3-*nitrodiphenyl*.—5 G. of 3-nitrodiphenyl were ground into a paste with 0·5 g. of ferric chloride, and 7 g. of bromine added. After the mass had cooled, water was added and the whole heated on the water-bath for 30 minutes. The product separated from

alcohol in plates, m. p. 95° (yield, almost theoretical) (Found : Br, 28·85. $C_{12}H_8O_2NBr$ requires Br, 28·8%).

4′-Bromo-3-aminodiphenyl was obtained on the reduction of the nitro-compound with stannous chloride in alcoholic hydrochloric acid solution. It separated from dilute alcohol in needles, m. p. 105° (Found : Br, 31·95. $C_{12}H_{10}NBr$ requires Br, 32·2%).

On acetylation of the base in pyridine solution *4′-bromo-3-acetamidodiphenyl* was obtained. It separated from alcohol in needles, m. p. 193° (Found : Br, 27·55. $C_{14}H_{12}ONBr$ requires Br, 27·75%). The base on oxidation with chromic anhydride in glacial acetic acid solution yielded *p*-bromobenzoic acid (m. p. 252°).

2 : 4 : 4′ : 6-*Tetrabromo-3-aminodiphenyl.*—2 G. of the monobromo-base and 5 g. of fused sodium acetate were dissolved in 50 c.c. of acetic acid. Excess of a 10% solution of bromine in acetic acid was added and the mixture gently warmed. The product, which separated on pouring into water, crystallised from alcohol in needles, m. p. 104° (Found : Br, 66·2. $C_{12}H_7NBr_4$ requires Br, 66·0%). On oxidation, in glacial acetic acid solution, with chromic anhydride, bromine was liberated and *p*-bromobenzoic acid (m. p. 251°) was isolated. Three bromine atoms must therefore be in the same ring as the amino-group, and the structure assigned depends partly on the direct bromination of 3-aminodiphenyl (see p. 3007).

3 : 4′-*Dinitrodiphenyl.*—A solution of 15 g. of 3-nitrodiphenyl in 250 c.c. of nitric acid (*d* 1·5) was kept over-night. The product, which separated when the mixture was poured into water, was digested with 500 c.c. of boiling methyl alcohol, the suspension allowed to cool, and the solid separated. It crystallised from acetone in pale yellow needles which melted, alone or mixed with the product of deamination of 3 : 4′-dinitro-4-aminodiphenyl (compare Scarborough and Waters, this vol., p. 1139), at 189°. Yield, 11—12 g.

2′ : 3-Dinitrodiphenyl was obtained on evaporation of the methyl alcohol used for the digestion of the crude nitration product. It separated from dilute acetic acid in white plates, m. p. 120° (compare Cain, J., 1912, **101**, 2298). Yield, 5—6 g. (Found : N, 11·5. Calc. : N, 11·5%). The structure of the compound was determined in the following manner : 2′ : 3-Dinitrobenzidine (Le Fèvre and Turner, J., 1926, 1759) was deaminated by grinding it to a paste with concentrated sulphuric acid, adding a little water and an excess of finely powdered sodium nitrite, followed by alcohol, and boiling the suspension under reflux for 30 minutes. The alcohol was partly removed and the dinitrodiphenyl separated. Crystallised from methyl alcohol and then from dilute acetic acid, it melted at 119° alone or mixed with the product of direct nitration.

2′ : 3 : 4 : 4′-*Tetranitrodiphenyl* was prepared by dissolving 2·5 g. of either 2′ : 3- or 3 : 4′-dinitrodiphenyl in 60 c.c. of concentrated sulphuric acid and adding gradually 3 g. of finely ground potassium nitrate. The solution was kept over-night and then poured on crushed ice. The *tetranitro*-compound crystallised from methyl alcohol in pale yellow cubes, m. p. 173° (Found: C, 43·35; H, 1·8; N, 16·8. $C_{12}H_6O_8N_4$ requires C, 43·1; H, 1·8; N, 16·75%). When it was warmed with an excess of piperidine for 5 minutes, and the solution poured into dilute hydrochloric acid, 2′ : 3 : 4′-trinitro-4-piperidinodiphenyl separated; this crystallised from methyl alcohol in deep scarlet prisms, m. p. 143° (Found: C, 55·05; H, 4·4; N, 15·2. Calc.: C, 54·85; H, 4·3; N, 15·1%).

3-*Aminodiphenyl*.—A hot solution of 20 g. of 3-nitrodiphenyl in 200 c.c. of alcohol was added in portions to a solution of 120 g. of stannous chloride in 120 c.c. of hydrochloric acid, and the mixture refluxed for 4 hours. The tin double salt, which separated after removal of a part of the alcohol, was decomposed with 30% sodium hydroxide solution and the base was isolated by means of ether and distilled twice under diminished pressure (yield, 75%), b. p. 195°/15 mm., m. p. 30°.

3-Acetamidodiphenyl, prepared by refluxing a solution of the base in twice its weight of glacial acetic acid for 6 hours, separated from dilute alcohol in needles or small plates, m. p. 149°.

N-*Chloro*-3-*acetamidodiphenyl*.—10 G. of the acetyl derivative were suspended in a solution of 13 g. of sodium bicarbonate in 200 c.c. of water, and 150 c.c. of *N*-sodium hypochlorite added drop by drop with vigorous stirring. After 12 hours, the product was filtered off. It crystallised from light petroleum in masses of small needles, m. p. 87° (Found: available Cl, 14·1. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

4-*Chloro*-3-*acetamidodiphenyl*.—(a) *Conversion of the chloroamine*. The chloroamine was dissolved in alcohol and a few c.c. of acetic acid were added; the solution was refluxed for 30 minutes. The product separated from dilute alcohol in plates, m. p. 148°.

(b) *Direct chlorination of* 3-*acetamidodiphenyl*. Chlorine diluted with carbon dioxide was passed into a 2% solution of the acetyl derivative in acetic acid and in the presence of fused sodium acetate. After the theoretical gain in weight had been obtained, the solution was kept for some hours and then poured into water. The product, precipitated as a gum, after repeated crystallisations from methyl alcohol, separated in plates, m. p. 148° (Found: Cl, 14·5. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

On hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid 4-*chloro*-3-*aminodiphenyl hydrochloride* was obtained.

It separated from dilute hydrochloric acid in needles, m. p. 247° (decomp.) (Found: HCl, 15·45; total Cl, 29·4. $C_{12}H_{10}NCl,HCl$ requires HCl, 15·2; Cl, 29·6%).

The decomposition of the salt with dilute aqueous ammonia gave a viscous oil which could not be obtained in a pure state. The salt was converted by the usual methods into 3 : 4-dichlorodiphenyl (m. p. 46°), and this compound on oxidation with chromic and acetic acids yielded 3 : 4-dichlorobenzoic acid (m. p. 198°).

4-Bromo-3-acetamidodiphenyl.—5 G. of 3-acetamidodiphenyl and 5 g. of fused sodium acetate were dissolved in 50 c.c. of acetic acid and treated with 45 c.c. of a 10% solution of bromine in acetic acid. After 1 hour, the mixture was poured into water; the precipitate obtained crystallised from dilute alcohol in plates, m. p. 163° (Found: Br, 27·4. $C_{14}H_{12}ONBr$ requires Br, 27·55%). On hydrolysis with 10% alcoholic hydrobromic acid, the base was obtained as a dark oil which decomposed on distillation under diminished pressure and separated as an oil from the usual solvents. The crude amine was converted, by the usual methods, into 3 : 4-*dibromodiphenyl*, a faintly yellow oil, b. p. 215°/15 mm. (Found: Br, 51·0. $C_{12}H_8Br_2$ requires Br, 51·2%). On oxidation with chromic and acetic acids 3 : 4-dibromobenzoic acid was isolated (m. p. 228°).

4 : 6-*Dibromo-3-acetamidodiphenyl.*—A solution of 5 g. of 3-acetamidodiphenyl and 15 g. of sodium acetate in 100 c.c. of acetic acid was refluxed and treated with 12 g. of bromine in portions. The product, which separated as a gum when the mixture was poured into water, crystallised from methyl alcohol in needles, m. p. 149°. The yield was some 50% of the theoretical, the residue being a gum (Found: Br, 43·55. $C_{14}H_{11}ONBr_2$ requires Br, 43·35%).

On hydrolysis of the acetyl derivative with alcoholic hydrobromic acid, the free base was obtained as a dark oil. This was converted into 2 : 4-*dibromodiphenyl*, a faintly yellow, viscid oil, b. p. 235°/15 mm. (Found: Br, 49·9. $C_{12}H_8Br_2$ requires Br, 51·2%). On oxidation with chromic and acetic acids 2 : 4-dibromobenzoic acid (m. p. 169°) was isolated. The symmetry of the molecule prevents a definite proof of the 4 : 6-structure; but from steric considerations it is more probable than the 2 : 4-structure.

4-Bromo-3-aminodiphenyl Hydrobromide.—5 G. of 3-aminodiphenyl were dissolved in carbon tetrachloride and treated with 50 c.c. of a 10% solution of bromine in the same solvent. The precipitated hydrobromide was filtered off and triturated with a fresh quantity of bromine solution. It separated from dilute hydrobromic acid in needles, m. p. 255° (decomp.) (Found: Total Br, 49·9%

$C_{12}H_{10}NBr,HBr$ requires Br, 48·65%). The structure was determined by liberating the base with dilute aqueous ammonia and subsequent acetylation, 4-bromo-3-acetamidodiphenyl (m. p. 163°) being obtained.

2 : 4 : 6-*Tribromo-3-aminodiphenyl.*—(a) 5 G. of 4-bromo-3-aminodiphenyl were dissolved in 100 c.c. of carbon tetrachloride and treated with 3·5 g. of bromine. The product was separated, suspended in fresh carbon tetrachloride, and treated with 3 g. of bromine. The solid product crystallised from alcohol, containing a little ammonia, in small needles, m. p. 141°. (b) 5 G. of 3-aminodiphenyl and 20 g. of fused sodium acetate were dissolved in acetic acid and treated with 180 c.c. of a 10% solution of bromine in acetic acid. After 1 hour the product was precipitated by pouring the mixture into water (Found: Br, 58·85. $C_{12}H_8NBr_3$ requires Br, 59·1%).

On oxidation of the base with chromic anhydride in glacial acetic acid solution, bromine was liberated and the molecule completely destroyed.

2 : 4 : 6-*Tribromodiphenyl* was obtained from the amine by the usual methods. It crystallised from methyl alcohol in needles, m. p. 64° (Found: Br, 61·7. $C_{12}H_7Br_3$ requires Br, 61·4%). Since oxidation with chromic anhydride caused complete decomposition, no definite proof can be given that the third bromine atom enters the 2-position; from a comparison with the behaviour of 2 : 4 : 4′ : 6-tetrabromo-3-aminodiphenyl, however, it may be reasonably assumed that all three bromine atoms are in one nucleus.

4-*Nitro-3-acetamidodiphenyl.*—A solution of 5 g. of 3-acetamidodiphenyl in a mixture of 30 c.c. of glacial acetic acid and 10 c.c. of acetic anhydride was heated to 70°, a solution of 1·5 c.c. of nitric acid (*d* 1·5) in 5 c.c. of acetic acid added drop by drop, and the temperature maintained for a further 30 minutes. The product, precipitated as a gum when the mixture was poured on ice, was extracted at once with alcohol, from which it separated in silky, pale yellow needles (yield, about 50%), m. p. 115° (Found: N, 11·1. $C_{14}H_{12}O_3N_2$ requires N, 10·95%).

On hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid, 4-*nitro-3-aminodiphenyl* was obtained. It separated very slowly from dilute alcohol in orange needles, m. p. 116° (Found: N, 13·0. $C_{12}H_{10}O_2N_2$ requires N, 13·1%). The base on deamination yielded 4-nitrodiphenyl (m. p. 114°).

4′-*Nitro-3-acetamidodiphenyl.*—5 G. of 3-acetamidodiphenyl were dissolved in 100 c.c. of nitric acid (*d* 1·5) at 0°. After 15 minutes, the mixture was poured on ice, and the product, a gum, filtered off. After repeated crystallisations from alcohol, it separated in pale

yellow needles, m. p. 192° (yield, about 40%) (Found: N, 11·0. $C_{14}H_{12}O_2N_2$ requires N, 10·95%).

The acetyl derivative on hydrolysis yielded *4'-nitro-3-aminodiphenyl*, which separated from alcohol in long, orange needles, m. p. 137° (Found: N, 12·95. $C_{12}H_{10}O_2N_2$ requires N, 13·1%), and on oxidation with chromic and acetic acids yielded *p*-nitrobenzoic acid (m. p. 238°).

4-Bromo-4'-nitro-3-acetamidodiphenyl.—A solution of 5 g. of 4-bromo-3-acetamidodiphenyl in 100 c.c. of nitric acid (*d* 1·5) was kept for 20 minutes and then poured on ice. The product was immediately extracted with methyl alcohol, from which it separated slowly, on dilution, in yellow needles, m. p. 158° (yield, about 40%) (Found: N, 8·4. $C_{14}H_{11}O_3N_2Br$ requires N, 8·35%).

By the hydrolysis of this acetyl derivative with 10% alcoholic hydrochloric acid, *4-bromo-4'-nitro-3-aminodiphenyl* was obtained. It separated from dilute methyl alcohol in red needles, m. p. 145° (Found: N, 9·7. $C_{12}H_9O_2N_2Br$ requires N, 9·55%). The base on oxidation with chromic anhydride yielded *p*-nitrobenzoic acid (m. p. 238°).

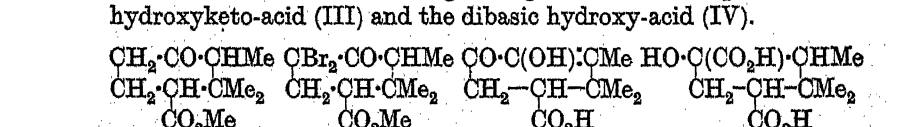
The authors beg to thank the Chemical Society for a grant from the Research Fund.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, August 29th*, 1927.]

CCCCI.—*Derivatives of Methyl* 2:2-*Dimethylcyclopentan*-3-*one*-1-*carboxylate.*

By CHARLES STANLEY GIBSON, KELVOI VENKATAKRISHNA HARIHARAN, and JOHN LIONEL SIMONSEN.

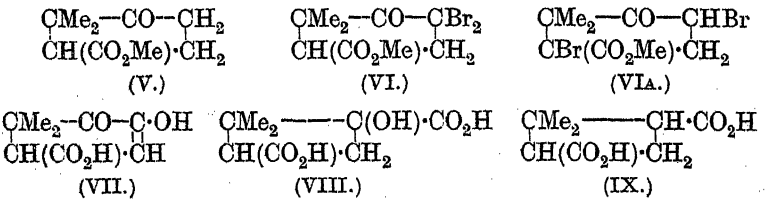
IT was shown recently that when methyl 2:2:3-trimethyl*cyclo*hexan-4-one-1-carboxylate (I) (J., 1925, **127**, 1294; this vol., p. 77) was brominated it yielded the dibromo-ester (II) and that this ester on treatment with alkali gave together with other products the hydroxyketo-acid (III) and the dibasic hydroxy-acid (IV).



(I.) (II.) (III.) (IV.)

It has appeared to us of interest to investigate whether *methyl* 2:2-*dimethylcyclopentan*-3-*one*-1-*carboxylate* (V) would on treatment with bromine and alkali behave in a similar manner, yielding the

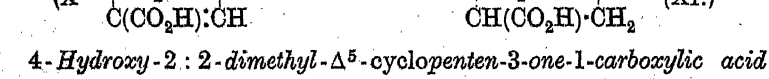
dibromo-ester (VI), the hydroxyketo-acid (VII) and a dibasic hydroxy-acid (VIII). The latter acid would be of particular importance, being the hydroxy-acid related to norpinic acid (IX), the synthesis of which has still to be effected.



(V.) (VI.) (VIA.)

(VII.) (VIII.) (IX.)

2 : 2-Dimethyl*cyclo*pentan-3-one-1-carboxylic acid was prepared by Perkin and Thorpe (J., 1904, **85**, 138), and by a modification of their process we have devised a method for obtaining it in excellent yield. When the *methyl* ester was brominated in acetic acid solution a crystalline *dibromo-ester* was obtained which is probably best represented by formula (VI); it is, however, not impossible that, in accordance with Wallach's views (*Annalen*, 1918, **414**, 296), the correct representation is by formula (VIA), and this will be further discussed below. This ester was readily acted upon by alkali, the main product of the reaction being a crystalline acid, $C_8H_{10}O_4$, m. p. 150—152°. There can be no doubt that this acid is represented by formula (X) for the following reasons: it gives a deep brown coloration with ferric chloride in aqueous solution and its alkaline solution is immediately oxidised by potassium permanganate; further, when oxidised with dilute nitric acid, it yields a mixture of dimethylmalonic acid and oxalic acid.



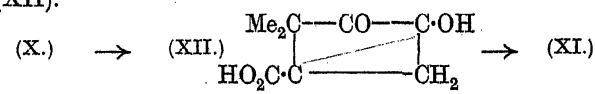
(X) (XI.)

4-*Hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid* can, however, also react in its tautomeric form as the diketo-acid (XI), since on treatment with semicarbazide acetate it yields a *disemicarbazone* and with *o*-phenylenediamine a *quinoxaline* derivative. The ketohydroxy-acid showed no tendency to yield a lactone, giving with acetyl chloride a liquid acetyl derivative, and when it was distilled under diminished pressure, apart from the formation of an oil which was probably 3 : 3-*dimethyl*cyclo*pentane*-1 : 2-*dione*, the greater part of the acid was recovered unchanged. On titration, the acid behaved like a dibasic acid, the hydroxy-group being evidently activated by the adjacent carbonyl group.

Since the conversion of (XI) into (X) must proceed through the intermediate stage of (VII)—an example of $\alpha\beta$: $\beta\gamma$-tautomerism—an attempt was made to find the acid (VII) amongst the products

of the action of alkali on the dibromo-ester. An oil was separated which, unlike the Δ^5-acid, gave with ferric chloride a red coloration. This acid, which could not be obtained crystalline, gave on boiling with alkali a quantity of the crystalline Δ^5-acid, and on treatment with semicarbazide acetate and with *o*-phenylenediamine the disemicarbazone and the quinoxaline derivative of the diketo-acid were obtained. There seemed to be little doubt, therefore, that this liquid acid consisted essentially of *4-hydroxy-2 : 2-dimethyl-*Δ^4*-cyclopenten-3-one-1-carboxylic acid*, and this view was confirmed by the formation of *as*-dimethylsuccinic acid on oxidation with dilute nitric acid.

The possibility that the constitution of the dibromo-ester should be represented by formula (VIA) remains to be investigated by studying the mechanism of the conversion of the Δ^5-acid (X) into the diketo-acid (XI), which may proceed by intramolecular tautomerism through the intermediate stage of the dicyclic ketohydroxy-acid (XII).



A large number of experiments were carried out with the object of converting both the Δ^4- and the Δ^5-acid into the dibasic hydroxy-acid (VIII), but no evidence of its formation has been obtained. Whether this is due to an actual inability of the *cyclo*pentane ring to pass into a *cyclo*butane ring or to the particular substituted ring used will form the subject of future experiments, which will also include the stereochemical investigation of the Δ^5-acid itself.

EXPERIMENTAL.

Ethyl βγ-*Dicyano*-β-*methylpentane*-γε-*dicarboxylate*.—To a solution of sodium (2·3 g.) in alcohol (30 g.), ethyl αβ-dicyano-β-methylbutyrate (18 g.) was added, the solution cooled, and ethyl β-iodopropionate (23 g.) gradually added, care being taken to avoid a rise of temperature (which produces a considerable quantity of ethyl acrylate). After remaining for 1 hour, during which time the temperature rose to about 40°, the reaction mixture was heated on the water-bath for 2 hours, water was then added, and the condensation product was isolated by extraction with ether and purified by distillation under diminished pressure. The whole distilled between 170° and 190°/5 mm. and on redistillation a large fraction was obtained, b. p. 184°/5 mm. (yield, 22 g.). *Ethyl* βγ-*dicyano*-β-*methylpentane*-γε-*dicarboxylate* is a faintly yellow, viscid oil with a somewhat unpleasant smell (Found: N, 9·8. $C_{14}H_{20}O_4N_2$ requires N, 10·0%).

β-*Methylpentane*-βγε-*tricarboxylic Acid*.—The dicyano-ester was

mixed with an equal volume of concentrated sulphuric acid, excessive rise of temperature being avoided, and when the mixture had cooled water was added until the solution was turbid. The hydrolysis was completed by boiling until evolution of carbon dioxide ceased and all the alcohol had evaporated, water being added from time to time to prevent charring (15 hrs.). From the cooled solution saturated with ammonium sulphate, the tricarboxylic acid was isolated by repeated extraction with ether. After crystallisation from hydrochloric acid it decomposed at 153—155°, but, as has been mentioned previously (*loc. cit.*, p. 1302), the m. p. is dependent on the rate of heating (Found: C, 49·8; H, 6·5. Calc.: C, 49·5; H, 6·4%).

The triethyl ester was obtained in a poor yield on esterification with alcohol and sulphuric acid; b. p. 161°/4 mm. (Found: C, 59·6; H, 8·6. Calc.: C, 59·6; H, 8·6%).

Ethyl 3 : 3-*Dimethylcyclopentan*-2-*one*-1 : 4-*dicarboxylate*.—Ethyl β-methylpentane-βγε-tricarboxylate (37 g.) was added to a suspension of finely divided sodium (5·6 g.) in benzene (100 c.c.), and the mixture warmed on the water-bath. A vigorous reaction took place and proceeded nearly to completion after removal of the source of heat; the last traces of sodium were dissolved by boiling for 1 hour. The deep brown solution was mixed with ice and made faintly acid with dilute sulphuric acid, and the benzene was separated, washed with sodium carbonate solution,* dried, and evaporated. The residual oil was distilled under diminished pressure; *ethyl* 3 : 3-*dimethylcyclopentan*-2-*one*-1 : 4-*dicarboxylate* was then obtained as a colourless oil, b. p. 145°/4 mm. (yield, 70%) (Found: C, 60·5; H, 8·1. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8%). An alcoholic solution of the ester gave with ferric chloride a violet coloration.

2 : 2-*Dimethylcyclopentan*-3-*one*-1-*carboxylic Acid*.—The keto-ester was boiled with sulphuric acid (100 c.c.; 5%) under reflux for 6 hours. After addition of sodium carbonate sufficient to render the solution alkaline, the alcohol was removed on the water-bath and the solution was acidified and extracted with ether. On removal of the solvent the keto-acid crystallised immediately and had m. p. 108—109° as stated by Perkin and Thorpe (*loc. cit.*).

The *methyl* ester (V), prepared in the usual manner, had b. p. 158°/100 mm. (Found: C, 63·7; H, 7·9. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%).

Bromination of Methyl 2 : 2-*Dimethylcyclopentan*-3-*one*-1-*carboxylate*. *Methyl* 4 : 4-*Dibromo*-2 : 2-*dimethylcyclopentan*-3-*one*-1-*carboxylate* (VI).—A solution of the ester (17 g.) in acetic

* The sodium carbonate solution on acidification yielded a small quantity of a viscid oil which was not examined.

acid (17 c.c.) was kept at 5—10° while bromine (32 g.) in acetic acid (10 c.c.) was gradually added. The bromine was very rapidly absorbed with evolution of hydrogen bromide. When the addition was complete the mixture was poured on ice. A heavy oil was deposited which solidified. The *bromo*-ester crystallised from dilute methyl alcohol or dilute formic acid in long prisms, m. p. 76—77° (yield, 86%) (Found: Br, 48·8. $C_9H_{12}O_3Br_2$ requires Br, 48·8%).

Action of Barium Hydroxide on Methyl 4 : 4-*Dibromo*-2 : 2-*dimethylcyclopentan*-3-*one*-1-*carboxylate*.—To the bromo-ester (34 g.) a hot solution of barium hydroxide (96 g.) in water (250 c.c.) was added, and the reaction mixture boiled under reflux. A vigorous action ensued and in order to avoid loss of material it was necessary to remove the source of heat. The hydrolysis was completed by boiling for 45 minutes, and the pale yellow solution was then evaporated on the water-bath until free from alcohol, acidified, and repeatedly extracted with ether. On removal of the solvent a crystalline cake remained (17 g.). This was mixed with benzene (50 c.c.) and after digestion allowed to remain over-night in the ice-chest; the acid which was insoluble in benzene was then collected and the filtrate (A) reserved for later investigation.

The acid (m. p. 148—150°) crystallised from hydrochloric acid in glistening prisms, m. p. 150—152° (slight decomp.) (Found: C, 56·0; H, 5·9. $C_8H_{10}O_4$ requires C, 56·4; H, 5·9%).

4-*Hydroxy*-2 : 2-*dimethyl*-Δ^5-*cyclopenten*-3-*one*-1-*carboxylic acid* (X) was readily soluble in water, acetone, ethyl acetate and formic acid, very sparingly soluble in benzene, toluene, and light petroleum, somewhat more soluble in chloroform. It gave a brown coloration with ferric chloride and immediately decolorised alkaline potassium permanganate. In chloroform it rapidly absorbed bromine, but the bromo-acid decomposed with evolution of hydrogen bromide. From its deep yellow solution in concentrated sulphuric acid the acid could be recovered unchanged. On titration with alkali and phenolphthalein it behaved as a dibasic acid, but the end-point was not quite sharp (Found: *M*, 176. Calc.: *M*, 170). The acid decomposed when heated above its melting point, but it distilled under diminished pressure largely unchanged and showed no tendency to lactone formation. A small quantity of a neutral yellow oil was separated (b. p. 80—100°/4 mm.) which gave a deep red colour with ferric chloride and showed weakly acidic properties. The oil, which was readily soluble in water, yielded a resinous semicarbazone and a liquid phenylhydrazone. With *o*-phenylenediamine it gave an oil which appeared to be a quinoxaline derivative and it also gave a sparingly soluble, oily benzoyl deriv-

ative. Although, therefore, it was not possible to characterise the oil, there can be little doubt that it consisted of 3 : 3-*dimethyl*cyclo*pentane*-1 : 2-*dione* or its tautomerides.

When the ketohydroxy-acid (X) was digested with acetyl chloride it yielded an oil which was sparingly soluble in water but readily soluble in sodium bicarbonate solution. The oil was precipitated unchanged from the alkaline solution on acidification and doubtless consisted of 4-*acetoxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid*. On treatment with semicarbazide acetate it underwent hydrolysis, yielding the disemicarbazone described below.

The ketohydroxy-acid was recovered unchanged after prolonged digestion with potassium hydroxide solution (10%); on treatment with more concentrated alkali solutions or on fusion with potassium hydroxide at 200° some resinification took place with formation of deep red solutions, but the bulk of the acid was recovered unchanged.

The *disemicarbazone* of 2 : 2-*dimethyl*cyclo*pentane*-3 : 4-*dione*-1-*carboxylic acid* (XI) crystallised from dilute alcohol in needles, decomp. 200—201° (Found : C, 42·1; H, 5·5; N, 29·1. $C_{10}H_{16}O_4N_6$ requires C, 42·3; H, 5·6; N, 29·6%).

The *quinoxaline* derivative was prepared by boiling an alcoholic solution of the acid with an excess of *o*-phenylenediamine. It separated from benzene in pale yellow, irregular plates, m. p. 175—177° (Found : C, 69·2; H, 6·0. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%).

Oxidation of 4-*Hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic Acid with Nitric Acid*.—The ketohydroxy-acid (2 g.) was heated with nitric acid (*d* 1·2; 20 c.c.) on the water-bath for 12 hours, nitric acid (*d* 1·4; 5 c.c.) was added, and the mixture heated for a further 3 hours. After removal of the excess of mineral acid on the water-bath, during which process a small quantity of a volatile organic acid was evaporated with the steam, an oil remained which partly crystallised. An aqueous solution of the acid was treated with an excess of calcium chloride to remove oxalic acid and the filtrate was extracted with ether. On removal of the solvent, a solid cake remained which after crystallisation from hydrochloric acid decomposed at 187°. This acid was identified as dimethylmalonic acid by the method of mixed m. p. and by titration (Found : *M*, 133. Calc. : *M*, 132).

4-*Hydroxy*-2 : 2-*dimethyl*-Δ^4-cyclo*penten*-3-*one*-1-*carboxylic Acid* (VII).—The benzene solution (A) (see p. 3013) yielded on removal of the solvent a viscid brown oil which could not be induced to crystallise. It was readily soluble in water, gave a deep red coloration with ferric chloride, and immediately decolorised alkaline potassium permanganate. On treatment with semicarbazide acetate

and with *o*-phenylenediamine it yielded the derivatives of the diketo-acid described above. When it was boiled for some hours with a solution of potassium hydroxide (10%) partial conversion into the Δ^5-acid took place. It gave a liquid acetyl derivative and showed no tendency to lactone formation.

When the oil was oxidised with dilute nitric acid under the conditions used for the oxidation of the Δ^5-acid, *as*-dimethylsuccinic acid was obtained, m. p. 140—141°. This was identified by the method of mixed m. p. and by the preparation of the characteristic, sparingly soluble calcium salt.

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), LONDON, S.E. 1.

INDIAN INSTITUTE OF SCIENCE, BANGALORE.

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CCCCII.—*The Colouring Matters of Carajura.*

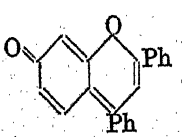
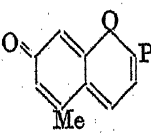
By ERNEST CHAPMAN, ARTHUR GEORGE PERKIN, and ROBERT ROBINSON.

CARAJURA (Crajura, Chica red) (Crookes, "Handbook of Dyeing and Calico Printing," 1874, p. 388; Schützberger, "Traité des Matières Colorantes," 1867, p. 412) is a rare red pigment, prepared by the Indians of the Rio Meta and the Orinoco from *Bignonia Chica* for use as a flesh paint (compare Humboldt's "Travels," Edinburgh, 1836, p. 229). It is stated that the leaves, which on drying acquire a red colour, are extracted with water and that the extract is treated with a ground bark called *aryane*, which effects the precipitation of the colouring matter. This process is strongly suggestive of the enzymic hydrolysis of a glucoside. The yield is small and the preparation tedious, and for this reason the material appears to be of a costly character. Erdmann (Crookes, *op. cit.*) recognised the pigment nature of chica and stated that, after treatment with acid, it dyes mordanted cotton in shades similar to those derived from lac dye. He considered that the colouring matter was an isomeride of anisic acid and assigned to it the formula $C_8H_8O_3$.

The material employed in this investigation, obtained through the kindness of Messrs. Wright, Layman, and Umney, consisted of dull red fragments enclosed in crudely woven oblong bags, evidently of native production. It possessed a peculiar camphoraceous odour, was insoluble in water, alcohol, and dilute aqueous alkalis, and thus differed from that described by Crookes (*op. cit.*) as soluble in 36% alcohol and dilute aqueous alkalis. Examination of the sample of carajura showed that it was a very crude product con-

taining approximately 4% of colouring matter as calcium or magnesium lake, peaty organic matter, perhaps "aryane" (23%), in addition to a wax and a coloured resin in small relative amount. The mineral matter as ash (38%) consisted mainly of lime, magnesia, and silica together with some potassium carbonate. Some part of the calcium appears to be present as oxalate. A preliminary account of the isolation and properties of carajurin, the main crystallisable colouring matter of carajura, has already been published (Perkin, P., 1914, **30**, 212), but as the results of later work the empirical formula of carajurin is considered to be $C_{17}H_{14}O_5$ instead of $C_{18}H_{16}O_5$, as then suggested.

Carajurin, of which only 10 g. have been available for this investigation, crystallises from benzene in garnet-coloured, prismatic needles; it has phenolic properties and contains two methoxyl groups, so the formula may be expanded to $C_{15}H_7O_2(OH)(OMe)_2$. The most characteristic property of the substance is the ease with which it combines with acids, yielding well-defined, crystalline, orange-red oxonium salts from which the base may be easily recovered. For example, the sulphate, $C_{17}H_{14}O_5,H_2SO_4$, crystallises from dilute sulphuric acid in orange needles but is decomposed on boiling with water, and the hydrochloride loses hydrogen chloride at 100°. The analogy existing between carajurin and the hydroxybenzopyranol bases prepared by Bülow and his collaborators has already been commented upon ("The Natural Organic Colouring Matters," Perkin and Everest, 1918, p. 343) and is indeed striking; physically, carajurin closely resembles anhydro-7-hydroxy-2 : 4-diphenylbenzopyranol (1 : 4) (I) (Bülow and Sicherer, *Ber.*, 1901, **34**, 2380), which crystallises from benzene. A third crystalline member of the group has been recently obtained by Hirst (this vol., p. 2490) and this (II) exhibits a still closer resemblance to carajurin.

(I.)   (II.)

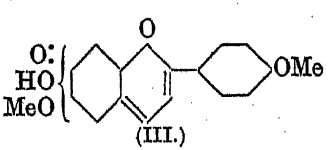
The composition of carajurin suggested that the connexion might be very close, because the colouring matter could be the anhydro-derivative of a dihydroxydimethoxyflavenol and thus be related to the large group of plant products that includes the flavones, flavonols, catechins, and anthocyanins. The coloured anhydrohydroxybenzopyranols have frequently been found to yield colourless derivatives of the hydroxybenzopyranols, and by the action of acetic anhydride and pyridine on carajurin a colourless *triacetyl* derivative, $C_{15}H_7O(OMe)_2(OAc)_3$, of hydrated carajurin was

obtained. Further confirmation of this view was found in the fact that fusion of carajurin with caustic alkali at 200° afforded *p*-hydroxybenzoic acid, whilst on boiling with concentrated aqueous potassium hydroxide, *p*-acetylanisole was obtained.

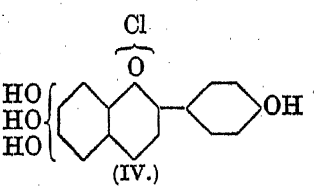
Bromination of carajurin in hot acetic acid solution gives, with remarkable ease, a compound, $C_{17}H_{12}O_5Br_4$ or $C_{17}H_{14}O_5Br_4$, which crystallises in orange needles and is apparently both a hydrobromide and a perbromide. On treatment with boiling acetone it is changed into *dibromocarajurin*, $C_{17}H_{12}O_5Br_2$, crystallising in bright red needles, bromoacetone being simultaneously produced.

Carajurin is completely demethylated on boiling with hydriodic acid and yields *carajuretin hydriodide*, $C_{15}H_{11}O_5I$, which has the composition and properties of a tetrahydroxyflavylium iodide. The action of cold pyridine on this salt leads to the formation of carajuretin, $C_{15}H_{10}O_5$, which occurs in scarlet needles and forms a colourless *penta-acetyl* derivative of hydrated carajuretin, $C_{15}H_7O(OAc)_5$.

On the supposition that the carajurin and carajuretin salts are flavylium derivatives it becomes of importance to note that these substances exhibit no tendency whatever to pass into pseudo-bases. Since the effect of a hydroxyl or methoxyl group in position 3 in the pyrylium nucleus in facilitating pseudo-base formation is well established, we concluded that carajurin is related to the flavone rather than to the flavonol group, that is, bearing in mind the formation of *p*-acetylanisole (above), that carajurin has the formula (III). Such a constitution, representing the substance as a



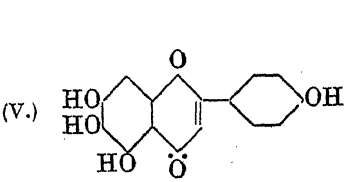
(III.)

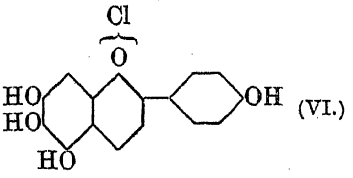


(IV.)

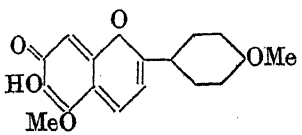
tetrahydroxybenzene derivative, served to explain the absence of phloroglucinol or other recognisable phenols from the alkali-fission products. Carajuretin hydrochloride, on this assumption, would conform to the type (IV), and in view of our strictly limited supply of the natural product we determined to synthesise flavylium salts of this nature in order to compare them with the carajuretin salts. The successful outcome of these synthetical investigations, which are described below, supplied the final proof of the correctness of the C_{17} formula for carajurin, and the fact that some of the salts which we prepared contain nuclear methyl groups is due to the uncertainty attached in the earlier stages to this question of the

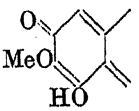
empirical formula. Guided by the assumed constitution of the flavone, scutellarein (V) (compare Bargellini, *Gazzetta*, 1915, **45**, i, 69; 1919, **49**, ii, 47), we prepared *scutellareinidin chloride* (VI) and

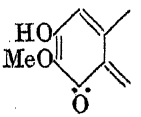

(V.)

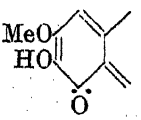

(VI.)

found that this salt was identical with carajuretin hydrochloride. This solved the major problem and left four possibilities for carajurin (VII, VIII, IX, X) differing only in the arrangement of substituents in the tetrahydroxybenzene nucleus; (VIII) and (IX) are tautomeric and would yield identical hydrochlorides (XI). This

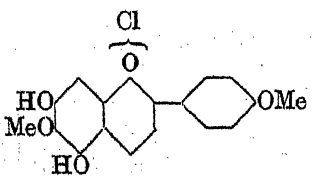

(VII.)

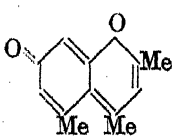

(VIII.)

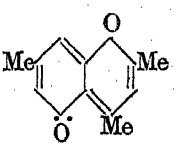

(IX.)


(X.)

5 : 7-dihydroxy-6 : 4′-dimethoxyflavylium chloride has been synthesised (see below) and it is not identical with carajurin hydrochloride. Moreover, the latter gives a ferric chloride colour reaction


(XI.)


(XII.)


(XIII.)

indicating the existence of vicinal hydroxyl groups in the salt; (XI) exhibits no such reaction. The choice between (VII) and (X) cannot yet be made definitely, but (VII) is preferable on account of the colour and stability of carajurin. The analogies already quoted support the formula (VII), whereas (X) should be a violet or blue substance. In making this statement we are taking cognisance of unpublished observations on the anhydro-bases from 5-hydroxyflavylium salts, which are violet or blue and characterised by instability. The only recorded work bearing on this point is that of Collie and White (J., 1915, **107**, 369), who condensed orcinol with acetylacetone in presence of hydrogen chloride and isolated two structurally different hydroxytrimethylbenzopyrylium chlorides, of

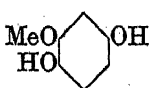
which one had a yellow and the other, obtained in smaller relative amount, an orange colour. The yellow salt gave a red quinonoid base (XII) and the orange salt gave a deep violet base (XIII). Provisionally, therefore, we suggest that carajurin has the formula (VII), and attempts to synthesise the colouring matter are in progress.

In addition to carajurin, carajura contains a second colouring matter, *carajurone*, $C_{15}H_9O_5 \cdot OMe$, which has been isolated in a micro-crystalline condition. This substance resembles carajurin in many of its properties, but is insoluble in benzene. It is probably a carajuretin monomethyl ether, but a clear proof of this is not available. Carajurin and carajurone dye mordanted fabrics in almost identical shades (see p. 3027), whereas those given by carajuretin are somewhat yellower. The red resin contained in carajura was not closely examined.

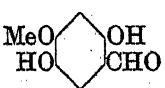
Derivatives of 1 : 2 : 3 : 5-*Tetrahydroxybenzene.*

The work involved in the synthesis of carajuretin necessitated the preparation of a number of partly methylated derivatives of 1 : 2 : 3 : 5-tetrahydroxybenzene and we have investigated more particularly those which may be used as the starting points of syntheses that can only proceed in one direction at each stage. We have had in mind not merely our immediate purpose but also the possibility of the synthesis, ultimately, of quercetagetin and gossypetin by such unambiguous methods.

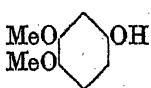
The readily accessible 2 : 6-dimethoxyquinol (XIV) was the



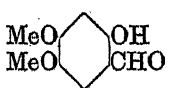
(XIV.)



(XV.)



(XVI.)



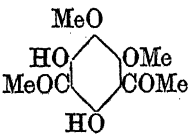
(XVII.)

starting point in many of our experiments; it could, for example, be directly condensed with anisoylacetone to a flavylium salt. On the other hand the introduction of the formyl group by Gattermann's method gave so poor a yield of the aldehyde (XV) that the process was useless for practical purposes. This was certainly due in part to the sparing solubility of dimethoxyquinol in ether, but also in all probability to its intrinsically small nuclear reactivity.

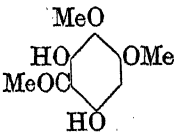
The methylation of dimethoxyquinol yields only antiarol (XVI) and tetramethoxybenzene, and we have confirmed the orientation of antiarol and worked out satisfactory conditions for its preparation. Antiarolaldehyde (XVII) could be obtained by an application of Gattermann's synthesis, but all attempts to prepare ketones such

as acetylantiarol and ω-methoxyacetylantiarol by the Hoesch method failed.

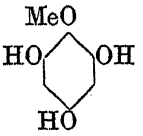
A series of experiments aiming at the *C*-acetylation of antiarol under varied conditions did not give the desired ketone, but two substances were isolated in small yield from the products of the action of aluminium chloride on antiarol and acetyl chloride in nitrobenzene solution. The first, m. p. 92—93°, gave analytical results agreeing with the formula (XVIII), whereas the second, m. p. 160—161°, is probably (XIX).



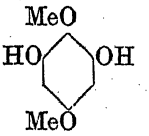
(XVIII.)



(XIX.)



(XX.)

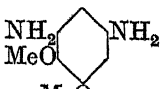


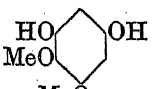
(XXI.)

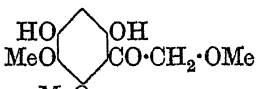
Bargellini and Bini (*Atti R. Accad. Lincei*, 1910, **19**, ii, 595; compare Bargellini, *Gazzetta*, 1919, **49**, ii, 47) isolated (*a*) tetramethoxyacetophenone, m. p. 48—50°, (*b*) a substance, m. p. 106—108°, regarded as 6-hydroxy-2 : 3 : 4-trimethoxyacetophenone, and (*c*) a substance, m. p. 162—163°, to which the formula (XIX) was assigned, from the products of interaction of 1 : 2 : 3 : 5-tetramethoxybenzene and acetyl chloride in carbon disulphide solution in presence of aluminium chloride. Repetition of the experiment gave (1) cream-coloured crystals, m. p. 177—178°, (2) yellow prisms, m. p. 111—112°, (3) brownish-yellow crystals, m. p. 162—163°, (4) 2 : 3 : 4 : 6-tetramethoxyacetophenone, m. p. 53—54°. The m. p. of a mixture of the substance, m. p. 160—161°, from antiarol with either (1) or (3) showed a large depression. It is hoped that further work will elucidate the nature of these substances and a detailed description is therefore postponed. It may also be pointed out that Nierenstein (J., 1917, **111**, 4) has ascribed the constitution (XIX) to a product, m. p. 166—168°, of the incomplete methylation of 2 : 3 : 4 : 6-tetrahydroxyacetophenone.

We have utilised iretol (XX) for the preparation of certain flavylium salts, although in this case the reactions could proceed in alternative directions. Investigation of the products showed that the hydroxyl in the *p*-position to the methoxyl group is the one which is involved in the ring closure. An interesting confirmation of this is found in the proof that the monomethyl ether of iretol, obtained by de Laire and Tiemann (*Ber.*, 1893, **26**, 2015) by treatment of the phenol with methyl-alcoholic hydrogen chloride, has the constitution (XXI). This and (XXIII) are the only possibilities and we have synthesised a dimethoxyresorcinol of the formula (XXIII) from 3 : 5-dinitroveratrole. A dilute aqueous solution of the hydro-

chloride of the corresponding diamine (XXII), containing a little stannous chloride, was boiled for many hours. The resulting phenol (XXIII) differs from de Laire and Tiemann's iretol monomethyl ether, a direct synthesis of which is being attempted.


(XXII.)

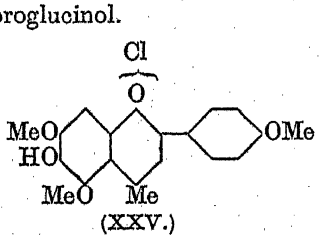

(XXIII.)

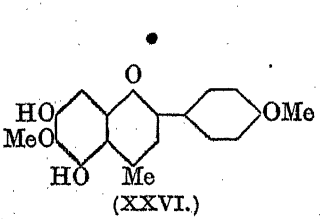

(XXIV.)

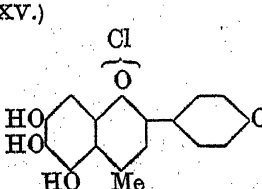
The dimethoxyresorcinols (XXIII and XXI) are the most suitable starting points in unambiguous syntheses of 3 : 5 : 6 : 7 : 3′ : 4′- and 3 : 5 : 7 : 8 : 3′ : 4′-hexahydroxyflavone, the constitutions, in all probability, of quercetagetin and gossypetin, respectively. In the former case we have demonstrated the feasibility of the scheme by the preparation of 2 : 4-dihydroxy-ω : 5 : 6-trimethoxyacetophenone (XXIV) from (XXIII) and methoxyacetonitrile in accordance with Hoesch's method (compare Slater and Stephen, J., 1920, **117**, 316). Test-tube experiments have convinced us that this ketone yields a flavonol derivative when it is heated with veratric anhydride and sodium veratrate (compare Allan and Robinson, J., 1924, **125**, 2192 and later communications).

Flavylium Salts derived from 1 : 2 : 3 : 5-*Tetrahydroxybenzene.*

Condensation of anisoylacetone and 2 : 6-dimethoxyquinol (XIV) in formic acid solution by means of hydrogen chloride gave (XXV), the alternative, a 4-anisyl-2-methylbenzopyrylium derivative, being excluded by the ready decomposition of the salt by alkalis with formation of *p*-acetylanisole and by analogy with the ascertained behaviour of benzoylacetone, for example, on condensation with phloroglucinol.


(XXV.)


(XXVI.)

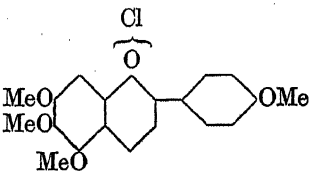

(XXVII.)

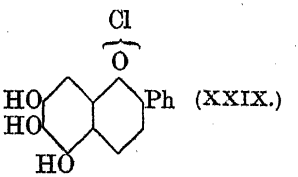
Anisoylacetone and iretol yield (XXVI) and on demethylation both

(XXV) and (XXVI) give 5 : 6 : 7 : 4′-*tetrahydroxy-4-methylflavylium chloride* (XXVII). Similarly 5 : 6 : 7 : 4′-*tetramethoxy-4-methylflavylium chloride* was obtained from antiarol and anisoylacetone.

The action of hydrogen chloride on a mixture of antiarolaldehyde (XVII) and *p*-acetylanisole in acetic acid solution led to the formation of 5 : 6 : 7 : 4′-*tetramethoxyflavylium chloride* (XXVIII); 5 : 7-dihydroxy-6 : 4′-dimethoxyflavylium chloride (XI) was obtained from iretol and anisoylacetaldehyde. On demethylation with hydriodic acid both salts (proof of structure of XI) gave *scutellareinidin iodide*; the *chloride* (VI) obtained from this was, as already stated, identified with carajuretin hydrochloride.

(XXVIII.)





(XXIX.)

Antiarolaldehyde, acetophenone, and hydrogen chloride yield 5 : 6 : 7-*trimethoxyflavylium chloride* and on demethylation the salt (XXIX) was obtained. This is the flavylium salt corresponding to the flavone baicalein (Shibata, Iwata, and Nakamura, *Acta Phytochim.*, 1923, **1**, 105; Bargellini, *Gazzetta*, 1919, **49**, ii, 47) and may be termed *baicaleinidin chloride*.

Experimental.

Carajurin.—Finely powdered carajura (100 g.) was extracted with boiling benzene to remove wax, which was found to interfere with the isolation of the colouring matters, and then digested with a mixture of water (600 c.c.) and concentrated hydrochloric acid (65 c.c.) at 95° for 15 minutes. After cooling, the dull red mass was collected, washed, and dried in the air and finally at 100° (A., 65 g.). Partial evaporation of the filtrate led to the separation of a red powder containing very little colouring matter and consisting chiefly of calcium oxalate; evaporation to dryness then gave a viscid residue containing organic matter and soluble salts of calcium, magnesium, and potassium, the former in preponderating amount.

The product A was extracted with boiling alcohol; the dull chocolate-coloured residue (ash, 26·5%) contained sand, and organic matter having a peaty nature. The orange-red alcoholic solution was evaporated to dryness on pure sand, and the powdered mass extracted with benzene for several hours in a Soxhlet apparatus (residue, B). The extract, after treatment with a little animal

charcoal, was filtered and concentrated; crystals were gradually deposited and the substance, after twice crystallising from benzene containing a trace of pyridine, was obtained in garnet-coloured needles, m. p. 205—207° (yield, 2·5 g.) (Found: C, 69·2, 68·6, 68·7, 68·1*, 68·1*; H, 4·7, 4·8, 4·9, 4·9*, 4·8* respectively; MeO, 19·8, 20·2, 20·6*, 20·4*, 20·5*. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1; 2MeO, 19·9%. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7; 2MeO, 20·8%).

Carajurin is sparingly soluble in hot benzene and alcohol, but is more readily soluble in pyridine; it does not dissolve in boiling dilute aqueous ammonia (distinction from carajuretin) and dissolves sparingly in dilute aqueous caustic alkalis to orange-red solutions which become brown on keeping. The solubility of carajurin in cold dilute aqueous sodium hydroxide is best demonstrated by its immediate complete extraction by the alkali from a dilute benzene solution. Carajurin and alcoholic lead acetate give a solution which slowly deposits pale red needles, whereas alcoholic ferric chloride gives a brownish-violet solution which becomes brown on the addition of an excess of the reagent.

Carajurin hydrogen sulphate. A hot solution of carajurin in acetic acid containing sulphuric acid gave a gelatinous precipitate on cooling, but when a trace of water was added to the hot liquid, fine, orange-yellow needles separated; these were collected and washed with acetic acid (Found: C, 50·7; H, 4·4. $C_{17}H_{14}O_5,H_2SO_4$ requires C, 51·5; H, 4·1%). Further analyses gave conflicting results, but owing to the necessity for conserving our material the matter was not pursued. The salt is readily soluble in boiling water, but decomposition occurs and the solution soon deposits red crystals of carajurin, m. p. 204—206°.

The *hydrochloride* crystallises from acetic acid in glistening, orange leaflets and from 8% hydrochloric acid in woolly balls of orange filaments which, when quickly heated, darken at 120° and partly fuse at about 196°, becoming black. On prolonged heating at 100° or on boiling with water it yields carajurin. It is, however, stable in aqueous solution in the presence of a slight excess of hydrochloric acid.

Action of Bromine on Carajurin.—When a solution of bromine (0·4 g.) in acetic acid (2·1 c.c.) was added to one of carajurin (0·23 g.) in boiling acetic acid (18 c.c.), crystals at once separated (yield, 0·46 g.) (Found: Br, 50·8. $C_{17}H_{14}O_5Br_4$ requires Br, 51·7%). The glistening, orange-red leaflets darkened at 195° and had become a black powder at 300°; on boiling with water, hydrogen bromide passed into solution. This tetrabromide (0·3185 g.) dissolved when boiled with acetone (10 c.c.), but red needles quickly separated and

* Indicates micro-analysis throughout.

the odour of bromoacetone became apparent. The product (yield, 75·3% of the weight of tetrabromide; in another experiment, 74·1%) evidently consisted of a dibromocarajurin (Found: Br, 35·2. $C_{17}H_{12}O_5Br_2$ requires Br, 35·2%); it did not melt, but became a carbonaceous mass at 300°. It dissolved in dilute alkalis to red solutions that became brown on keeping. Theoretically a carajurin tetrabromide (or a dibromocarajurin dibromide, $C_{17}H_{12}O_5Br_4$) should give 74% of its weight of dibromocarajurin.

A curious result was obtained when the bromination was effected in commercial acetic acid solution, red needles, apparently consisting of a crude tribromocarajurin, being isolated (Found: Br, 46·4. Calc.: Br, 44·9%).

Fission of Carajurin with Alkalis.—By fusing carajurin with 10 parts of sodium hydroxide and a little water at 200°, dissolving the melt in water, acidifying the solution and extracting it with ether, a crystalline product was obtained containing *p*-hydroxybenzoic acid and a colourless, crystalline substance, m. p. 185—187°, which was sparingly soluble in water and gave no coloration with ferric chloride.

A dilute solution of carajurin in dilute aqueous-alcoholic potassium hydroxide was rapidly distilled. The red liquid became orange-yellow (opening of the heterocyclic ring) and at a later stage a dark oil separated. When the alkali became quite concentrated, a colourless oil distilled in the steam, and this was isolated by means of ether and identified as *p*-acetylanisole by conversion into the semicarbazone, m. p. 197°, alone or mixed with an authentic specimen.

O-*Triacetyldihydrocarajurinol.*—The red solution of carajurin (0·2 g.) and pyridine (0·6 c.c.) in acetic anhydride was kept for 3 days and then mixed with ice-cold dilute sulphuric acid. The pink precipitate was collected, washed, dried in the air, and dissolved in a very small volume of hot acetone. Crystals (0·07 g.) separated on keeping, and were obtained, on recrystallisation from methyl alcohol (charcoal), in colourless leaflets, m. p. 142° (Found*: C, 62·3; H, 5·1. $C_{23}H_{22}O_9$ requires C, 62·4; H, 5·0%). When this substance was boiled with a mixture of alcohol and concentrated hydrochloric acid, an orange-yellow solution of an oxonium salt was obtained; the addition of sodium acetate produced a red colour, and the pigment (probably carajurin) could be extracted by benzene, giving a red solution.

A second acetylated carajurin derivative, probably *O*-acetylcarajurin, was obtained by the prolonged action of cold acetic anhydride and a trace of sulphuric acid on the colouring matter; it crystallised in orange needles, m. p. 190—191°, but has not been closely examined.

Carajuretin.—After the methoxyl estimations (those carried out on the normal scale, not those in which Pregl's micro-method was used) the hydriodic acid was found to contain red needles of *carajuretin hydriodide*. These were collected, washed with sulphurous acid and then with water, and dried at 100° (Found: I, 31·6. $C_{15}H_{10}O_5$,HI requires I, 31·9%) (yield, 133·5% on the weight of carajurin employed. Calc., 134·1%). When hydriodic acid was added to a solution of this salt in hot alcohol, characteristic, fan-shaped clusters of fine, red needles separated.

The hydriodide dissolved at once in a small volume of cold pyridine and crystals soon separated from the solution; after the addition of boiling water and cooling, the scarlet needles were collected (yield, 68% on the weight of carajuretin hydriodide. Calc., 67·8%). The substance was recrystallised by concentrating a solution in much boiling alcohol and then adding boiling water, and *carajuretin* was thus obtained as a woolly mass of red needles that became black at 330° without exhibiting a melting point (Found: C, 66·7; H, 4·1. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%).

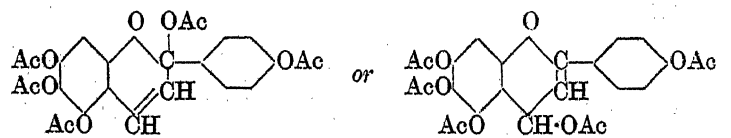
Carajuretin gives a fine crimson solution, becoming brown in the air, in aqueous ammonia or aqueous sodium carbonate. It gives a violet coloration with alcoholic ferric chloride, a dull reddish-violet precipitate with alcoholic lead acetate, and a deposit, probably of a monopotassium salt, with alcoholic potassium acetate. The substance combines with sulphuric acid in acetic acid solution to give the *hydrogen sulphate*, orange-yellow needles that can be crystallised from dilute sulphuric acid but are decomposed, with liberation of sulphuric acid (and probably carajuretin), on boiling with water.

The *hydrochloride* has been carefully examined for the sake of the comparison with the synthetical scutellareinidin chloride. Carajuretin hydriodide (0·9 g.) in hot alcoholic solution (100 c.c.) was decomposed by means of precipitated silver chloride. The filtered solution, mixed with a little hydrochloric acid, was concentrated; it then deposited prisms (0·53 g.) having an intense steel-blue lustre (Found* in material dried at 100°: C, 55·3, 55·5; H, 4·3, 4·2; Cl, 11·3, 11·0. $C_{15}H_{10}O_5$,HCl,H_2O requires C, 55·5; H, 4·0; Cl, 10·9%). The pure salt is sparingly soluble in alcohol to a brownish-orange solution; slightly impure specimens are readily soluble. Addition of a trace of ferric chloride to the alcoholic solution produces an intense brownish-violet coloration, which becomes reddish-brown on the addition of water. Addition of sodium carbonate to the alcoholic solution gives a fine permanganate-coloured liquid that becomes bluer on dilution with alcohol. The solution in aqueous sodium carbonate has a damson colour. The salt is sparingly soluble in cold 0·5% hydrochloric acid, but dissolves in the hot solvent.

on the addition of an equal volume of cold concentrated hydrochloric acid lustreless, woolly, orange needles are deposited, but if the liquid is heated, causing redissolution, and cooled very slowly, the substance separates completely in characteristic, elongated, rhombic prisms with a steel-blue lustre. These crystals are reddish-orange when viewed by transmitted light under the microscope and give a red smear on paper. Similarly the evaporation of an alcoholic solution of the chloride containing some 10% aqueous hydrochloric acid gives woolly needles that change in contact with the solvent into glistening, rhombic prisms. The salt is sparingly soluble in cold 7% sulphuric acid, but dissolves on heating: a gelatinous precipitate separates as the solution cools; on keeping, especially if warm, the amorphous material is replaced by very slender, orange-red needles. If aqueous perchloric acid (*d* 1·2) is added to the hot solution in 7% sulphuric acid, the *hydrogen perchlorate* quickly separates in clusters of short, orange-red needles exhibiting a bright metallic reflex.

The addition of bromine to a hot solution of carajuretin in acetic acid causes the immediate precipitation of minute, orange-red needles; these give hydrogen bromide to boiling water.

O-*Penta-acetyldihydrocarajuretinol*,



—A mixture of carajuretin (0·2 g.), pyridine (0·7 c.c.), and acetic anhydride (0·8 c.c.) was kept for 5 days; the red liquid was then added to ice-cold, dilute sulphuric acid and the pink precipitate was collected, washed, and dried on tile. An acetone solution of this product, after treatment with charcoal, was filtered and evaporated to dryness; the residue was dissolved in the minimum volume of boiling alcohol, and the solution allowed to cool. The cloudiness which then appeared was cleared by the addition of acetone drop by drop as required, and after 2 days the crystals (0·07 g.) were collected and twice recrystallised from benzene (charcoal). The colourless, prismatic needles, m. p. 156—157°, thus obtained were sparingly soluble in cold benzene and readily soluble in acetone (Found*: C, 60·3; H, 4·5. $C_{25}H_{22}O_{11}$ requires C, 60·2; H, 4·4%). This derivative discoloured on keeping in a specimen tube; it was reconverted into carajuretin hydrochloride by hydrolysis with alcoholic-aqueous hydrochloric acid and the characteristic lustrous, rhombic prisms of the salt were obtained. An acetyl estimation was carried out by Freudenberg's micro-

analytical method (*Annalen*, 1923, **433**, 230; Freudenberg and Weber, *Z. angew. Chem.*, 1925, **38**, 280) [Found: Ac, 42·8. $C_{15}H_7O(OAc)_5$ requires Ac, 43·2%].

Carajurone.—The residue B (see p. 3022) in the Soxhlet tube after removal of carajurin was extracted with boiling acetone and, after treatment with charcoal and filtration, the solution was concentrated to a small volume. Dark, granular material separated and this was washed with a little benzene and crystallised from acetone. *Carajurone* was thus obtained as an indistinctly crystalline, scarlet mass, m. p. 183—186° (decomp.) (Found* in material dried at 105° in a high vacuum: C, 67·1; H, 4·3; MeO, 11·6. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2; 1MeO, 11·1%) (an earlier analysis gave MeO, 11·4%).

Carajurone dissolves in aqueous sodium carbonate to a brownish-red solution, the colour of which is neither so intense nor so persistent on dilution as that obtained from carajuretin under similar conditions. The ferric chloride reaction in alcoholic solution closely resembles that given by carajurin; alcoholic lead acetate gives a maroon-coloured precipitate. The substance combines with strong acids, forming oxonium salts the solutions of which are brownish-orange, and there can be little doubt that it is carajuretin monomethyl ether. Definite evidence respecting the position of the methoxyl group, on this hypothesis, was not obtained, but the perceptible odour of *p*-acetylanisole observed on boiling a solution in concentrated aqueous sodium hydroxide is an indication that the methoxyl is in position 4'. The vapour evolved on destructive distillation of carajurone has an odour resembling that of *p*-hydroxybenzaldehyde.

Dyeing Properties.—Owing to its sparing solubility in water, crystalline carajurin dyes mordanted wool and cotton with difficulty; to overcome this, an alcoholic solution was poured into much water and satisfactory dyeings were then secured. The following comparative results were obtained on mordanted wool:

	Chromium.	Aluminium.	Tin.	Iron.
Carajurin.	Deep maroon.	Dull brownish-red.	Bright scarlet.	Deep violet-maroon.
Carajurone.	Deep maroon.	Dull brownish-red.	Dull scarlet.	Deep violet-maroon.
Carajuretin.	Brown.	Dull brownish-orange.	Brownish-scarlet.	Brownish-maroon.

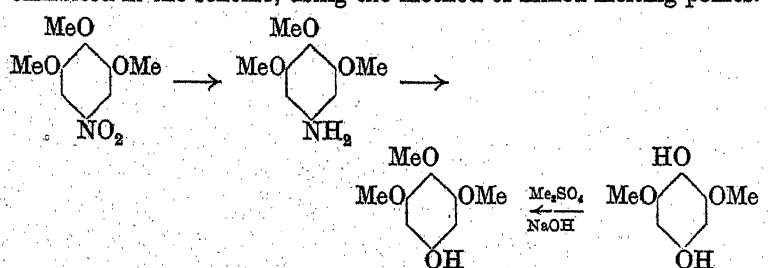
Pyrogallol Trimethyl Ether.—The following modification of Ullmann's method (*Annalen*, 1903, **327**, 116) for the methylation of pyrogallol gives an 86% yield of a colourless product that does not require the subsequent treatment with ether recommended by Ullmann.

Aqueous sodium hydroxide (150 c.c. containing 60 g. of sodium hydroxide) was gradually added from a tap-funnel during 3—4 hours to a mixture of pyrogallol (42 g.), methyl sulphate (189 g.), and alcohol (100 c.c.) agitated vigorously by means of a gas-tight stirrer and contained in a flask (reflux condenser) from which air was excluded by hydrogen. After the completion of the reaction the vessel was cooled in an ice-bath and the addition of water (150 c.c.) caused the separation of the ether in glistening, white prisms, m. p. 47°. The average yield in many experiments was 48 g.

Antiarol (XVI).—2 : 6-Dimethoxybenzoquinone (24 g.) was obtained by Graebe and Hess's method (*Annalen*, 1905, **340**, 237; compare Will, *Ber.*, 1888, **21**, 608) from nitric acid (*d* 1·2) in 95% alcohol and pyrogallol trimethyl ether (40 g.).

Dimethoxyquinol, m. p. 160° (literature, 158°), was obtained by reduction of the quinone in 87% yield. It is stated to be easily soluble in ether, but we found that 100 c.c. of dry ether dissolved only 0·4 g. of the phenol. It is readily soluble in acetone, the simple alcohols, and acetic acid in the cold, but it is very sparingly soluble in carbon disulphide, nitrobenzene, benzene, toluene, chloroform, *iso*amyl ether, and light petroleum in the cold. It is partly on this account that we experienced so much difficulty in the preparation of an aldehyde from this phenol.

Will (*loc. cit.*; compare Bargellini and Bini, *Gazzetta*, 1911, **41**, ii, 8) obtained a trimethoxyphenol as a by-product in the preparation of 1 : 2 : 3 : 5-tetramethoxybenzene by methylation of 2 : 6-dimethoxyquinol with methyl iodide and methyl-alcoholic potassium hydroxide. The constitution of this substance was apparently first determined by Schlör (*Diss.*, 1889; compare Graebe and Suter, *Annalen*, 1905, **340**, 224; Kiliani on antiarol from *antiaris toxicaria*, *Arch. Pharm.*, 1896, **234**, 444; Thoms and Siebelung, *Ber.*, 1911, **44**, 2124), and as it was a matter of considerable importance in the present investigation we confirmed the relations exhibited in the scheme, using the method of mixed melting points.



The following conditions were employed for the semi-methylation of 2 : 6-dimethoxyquinol, the object aimed at being the complete

conversion of the quinol into antiarol and tetramethoxybenzene, because both substances were required and the separation of antiarol from dimethoxyquinol was difficult. A solution of sodium hydroxide (20 g.) in water (140 c.c.) was added to 2 : 6-dimethoxyquinol (34 g.) in a flask from which air was excluded by hydrogen. Methyl sulphate (32 g.) was then added in one portion with vigorous shaking, which was continued for 10—15 minutes and at intervals for 1 hour. 11 G. of 1 : 2 : 3 : 5-tetramethoxybenzene were isolated, and the alkali-soluble fraction (20 g.) was crystallised from ten times its weight of water and thus obtained in flat, white needles, m. p. 146° (yield 16·5 g.), and free from unchanged dimethoxyquinol.

Sodium antiarolate crystallised in silky, snow-white needles when a solution of antiarol in moderately concentrated aqueous sodium hydroxide was cooled.

O-*Acetylantiarol* (3 : 4 : 5-*trimethoxyphenyl acetate*), obtained by the action of boiling acetic anhydride and sodium acetate on the phenol, crystallised from not too much alcohol in colourless, transparent, elongated prisms, m. p. 74° (Found: C, 58·5; H, 6·3; MeO*, 40·8, 40·8, 40·7. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2; 3MeO, 41·2%). The micro-analytical estimations of methoxyl in this readily purified substance gave slightly low results, and as those of carajurin were carried out in the same apparatus we considered that a similar small error would affect those determinations also. The first indication that carajurin has the formula $C_{17}H_{14}O_5$ rather than $C_{18}H_{16}O_5$ was obtained in this way.

3 : 6-*Dihydroxy*-2 : 4-*dimethoxybenzaldehyde* (XV).—Dry hydrogen cyanide in a stream of carbon dioxide and, by another delivery tube, a stream of hydrogen chloride, were simultaneously introduced into a warm solution of 2 : 6-dimethoxyquinol (3·5 g.) in ethyl acetate (100 c.c.). The slow passage of hydrogen chloride was continued for 2 hours and the flask was then stoppered and kept in the ice-chest. Next day, water was added to the reddish-green, dichroic solution so as to dissolve the small, dark-green deposit and the red, aqueous solution was then separated from the colourless ethyl acetate layer and boiled for a few minutes with passage of sulphur dioxide. On cooling, clumps of fine needles separated and these crystallised from hot water, containing sulphur dioxide, in very pale brown, feathery needles, m. p. 135—136° (Found: MeO*, 30·7. $C_9H_{10}O_5$ requires 2MeO, 31·3%). This substance, the yield of which was extremely poor, gives a sparingly soluble semicarbazone, and a golden-yellow solution in aqueous sodium hydroxide. It develops a green coloration, brown with excess of the reagent, on the addition of ferric chloride to its alcoholic solution.

Antiarolaldehyde (XVII).—In this experiment the use of sufficient

ether to dissolve the antiarol was found inadvisable and the quantities were so adjusted that all the phenol passed into solution before the separation of aldimine hydrochloride commenced. Hydrogen cyanide (from 10 g. of potassium cyanide), carried over in a slow stream of carbon dioxide, was introduced into a solution and suspension of finely powdered antiarol (6 g.) in anhydrous ether (300 c.c.), and a moderately rapid stream of hydrogen chloride led into the mixture (reflux condenser), which was frequently shaken. After 3 hours, glistening, white crystals began to be deposited and after 2 hours more, the stream of gas was interrupted and the vessel stoppered and kept over-night. The ethereal solution was decanted and the aldimine hydrochloride decomposed by heating on the steam-bath with water (30 c.c.) for a few minutes. The aldehyde, which separated as an oil and crystallised on cooling (4·7 g.), was recrystallised by the addition of warm water to its solution in hot methyl alcohol (yield, 4·45 g.). It was obtained in elongated, flat, white prisms, m. p. 65° (Found: C, 56·8; H, 5·8. $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%). *Antiarolaldehyde* is slightly soluble in boiling water to a colourless solution, which becomes turbid on cooling and then deposits beautiful, star-shaped aggregates of needles. It is readily soluble in ether, alcohol, benzene, chloroform, acetic acid, and acetone. In aqueous or alcoholic solution it develops an intense brownish-violet coloration on the addition of ferric chloride; its solution in aqueous sodium hydroxide has a greenish-yellow colour. The *semicarbazone*, prepared in the usual manner, crystallised from 80% alcohol in slender, colourless needles that became yellow at 210° and melted with effervescence at 245° (Found: N, 15·4. $C_{11}H_{15}O_5N_3$ requires N, 15·6%).

Iretol Monomethyl Ether (XXI).—Picric acid (50 g.) gave recrystallised picryl chloride (30 g.) according to Jackson and Gazzolo's method (*Amer. Chem. J.*, 1900, **23**, 384); the addition of benzene in the crystallisation from alcohol, recommended by these authors, was found to be unnecessary.

Jackson and Boos (*Amer. Chem. J.*, 1898, **20**, 444) showed that the scarlet compound obtained by the action of sodium methoxide on picryl chloride yields methyl picrate on decomposition with water, but the method does not appear to have been used for the preparation of the substance in quantity. The following conditions gave good results. Sodium (4 g.) was dissolved in methyl alcohol (120 c.c.), and the solution added with shaking to one of picryl chloride (20 g.) in methyl alcohol (40 c.c.). After a short time, 80—100 c.c. of the methyl alcohol were distilled away and hydrochloric acid was added to the residue until it became yellow (acid reaction). Precipitation of the ether was completed by water and after one

crystallisation of the product from 60 c.c. of methyl alcohol it had m. p. 67—68° (yield, 18 g.) (Buttle and Hewitt, J., 1909, **95**, 1759, assign the m. p. 68° to the pure ether).

The conversion of methyl picrate into iretol was carried out by Kohner's method (*Monatsh.*, 1899, **20**, 928), and de Laire and Tiemann's work (*loc. cit.*) on the monomethylation of iretol from irigenin was confirmed with the synthetical material.

4 : 5-*Dimethoxyresorcinol* (XXIII).—The nitration of 4-nitroguaiacol (Pollecoff and Robinson, J., 1918, **113**, 647) required very careful control and the following method was used. Nitric acid (100 c.c.; *d* 1·42), cooled in ice to 0—3°, was mechanically stirred, finely powdered 4-nitroguaiacol (10 g.) was added in one portion, and 50 c.c. of nitric acid (*d* 1·42) at 0° were used to wash the stirrer and the sides of the container. The temperature rose and when it reached 11—12°, usually in 2 or 3 minutes, a large volume of water was added, precipitating the dinitroguaiacol as a bulky, yellow, crystalline mass (yield, 10·5 g.; m. p. 121—122°; the pure substance has m. p. 123°).

The dinitroguaiacol (15 g.) gave 4 : 6-dinitroveratrole (13·5 g., m. p. 97—98°; the pure substance has m. p. 101—102°) when heated with potassium carbonate and methyl sulphate in nitrobenzene solution.

A mixture of 4 : 6-dinitroveratrole (15 g.), granulated tin (50 g.), concentrated hydrochloric acid (150 c.c.), and water (50 c.c.) was shaken, the reaction being started by gentle heating on the steam-bath, subsequently moderated by the addition of water (20—30 c.c.), and finally completed by short heating on the steam-bath. The filtered liquid was evaporated to dryness under diminished pressure, air having been displaced by carbon dioxide, and the residue was dissolved in water. After removal of tin as sulphide, the filtered solution was evaporated to dryness under the conditions previously employed, leaving a white, crystalline crust (15 g.). This gave the *m*-diamine reaction with nitrous acid and a purple coloration with ferric chloride in aqueous solution. A solution of this product (17 g.) and stannous chloride (3·5 g.) in air-free water (1000 c.c.) was refluxed for 48 hours in a stream of carbon dioxide. Tin was eliminated as sulphide from the filtered, yellowish solution and the liquid was then concentrated to about 150 c.c. under diminished pressure (of carbon dioxide) and extracted with ether. The combined extracts were dried with sodium sulphate and filtered and the solvent was removed, finally under diminished pressure, leaving a brown oil that solidified on rubbing and was found to be free from nitrogenous material. This was dissolved in a little water and lead acetate added, giving a small, flocculent precipitate. Lead

was eliminated as sulphide from the filtered solution, which was then evaporated to dryness under diminished pressure (carbon dioxide). The residue was dissolved in warm benzene; on slowly cooling, an oil separated; the benzene was decanted from this, and glassy crystals were then deposited. After recrystallisation from benzene the hard, transparent prisms, approximately tetrahedral in shape but possessing many facets, were dried in the air and then had m. p. 76—77°. When stored in an evacuated desiccator over calcium chloride, the crystals became at first sticky, adhering together, and then in a few days dry and friable again. The anhydrous material had m. p. 115—116° (Found*: C, 56·5; H, 5·9; MeO, 36·2. $C_8H_{10}O_4$ requires C, 56·4; H, 5·9; 2MeO, 36·5%). The solvent of crystallisation was also retained when the phenol was crystallised from chloroform; it was water, because, in a second experiment, the crude product was more thoroughly dried before the crystallisation from benzene and the crystals (1·1 g.) then melted at 105—110° and at 113° after recrystallisation.

The behaviour of this *dimethoxyresorcinol* with ferric chloride distinguishes it sharply from iretol monomethyl ether, the colorations developed in aqueous solutions being reddish-brown and blue respectively. A pine shaving, immersed in an alcoholic hydrochloric acid solution of the phenol, becomes mauve in colour.

Attempted Nuclear Acetylation of Antiarol.—There was no satisfactory outcome of experiments in which antiarol was (1) heated with acetic acid and zinc chloride, (2) treated with sulphoacetic acid at room temperature (compare Schneider and collaborators, *Ber.*, 1921, **54**, 1484, 2298, 2302; 1922, **55**, 1892), (3) boiled with acetic anhydride containing a little concentrated sulphuric acid (compare Brand and Collischonn, *J. pr. Chem.*, 1921, **103**, 338), (4) treated with acetyl chloride alone or in presence of anhydrous ferric chloride with or without carbon disulphide as solvent, (5) treated in anhydrous ether with acetonitrile (or methoxyacetonitrile) and hydrogen chloride, with or without the addition of zinc chloride.

Antiarol could not be carboxylated by means of potassium hydrogen carbonate, even in glycerol solution at 180° (stream of carbon dioxide) (compare Brunner, *Annalen*, 1907, **351**, 359); the phenol was recovered unchanged.

The relatively small nuclear reactivity of antiarol is of theoretical interest, a comparison with the much more reactive phloroglucinol dimethyl ether illustrating the depressing effect of the methoxyl group in the *m*-position to the free nuclear positions. An analogous phenomenon is the feeble reactivity of pyrogallol, in comparison with resorcinol, in the Hoesch reaction.

Acetyl chloride (10 c.c.) and then aluminium chloride (16 g.)

were added to a solution of antiarol (10 g.) in nitrobenzene (160 c.c.) and the mixture was heated for a short time on the steam-bath. The following products were isolated: (A). This was precipitated on addition of a little water to an alcoholic solution of the mixture; it crystallised from aqueous alcohol in stout, white needles, m. p. 92—93° (Found: C, 56·7, 56·7; H, 5·5, 5·7; MeO*, 24·1, 24·0. $C_{12}H_{14}O_6$ requires C, 56·7; H, 5·6; 2MeO, 24·4%). This substance, 4 : 5-*dimethoxy*-2 : 6-*diacetylresorcinol* (XVIII), is sparingly soluble in water, readily soluble in ether, and develops a deep red coloration with alcoholic ferric chloride. It dissolves in aqueous sodium hydroxide to a yellow solution and is not decomposed when the liquid is boiled.

After the separation of (A) a second substance (B) was isolated by taking advantage of its relatively sparing solubility in ether. It was only obtained in small amount, and crystallised from benzene in yellow prisms, m. p. 160—161° (Found*: MeO, 28·7, 28·9. $C_{10}H_{12}O_5$ requires 2MeO, 29·3%). (C) was obtained in minute amount from the ethereal solution, after separation of (A) and (B), in pearly plates, m. p. 78—84°, but owing to paucity of material it was not further investigated.

ω : 5 : 6-*Trimethoxyresacetophenone* (XXIV).—A solution of 4 : 5-dimethoxyresorcinol (0·75 g.) and methoxyacetonitrile (0·4 g.) in dry ether (30 c.c.) was saturated with hydrogen chloride and kept over-night. A clear solution resulted, but on the addition of fresh dry ether, colourless crystals were precipitated and these were separated and washed with ether. When an aqueous solution of this ketimine hydrochloride was heated on the steam-bath for a few minutes, the normal ready hydrolysis did not occur and ether extracted only a minute amount of the ketone. After being kept for several weeks, however, the aqueous solution gradually deposited yellow crystals, m. p. 128—129°. The substance crystallised from water in long, glistening, very pale yellow needles, m. p. 129—130° (Found*: C, 54·7; H, 5·9; MeO, 38·3. $C_{11}H_{14}O_6$ requires C, 54·5; H, 5·8; 3MeO, 38·4%). The ketone is readily soluble in alcohol and in boiling water; its solution in 10% aqueous sodium hydroxide is yellow, and after prolonged boiling, the unchanged substance, m. p. 129—130°, is recovered an acidification. The addition of ferric chloride to an alcoholic solution produces a holly-green coloration which fades to brown; in aqueous solution, the coloration is brownish-black.

Anisoylacetone.—Besthorn and Jaegli (*Ber.*, 1894, **27**, 810) employed alcohol-free sodium ethoxide for the condensation of *p*-acetylanisole and ethyl acetate. We have used sodamide as the condensing agent. Finely powdered sodamide (4 g.) was

added to a mixture of *p*-acetylanisole (15 g.), ethyl acetate (22 g.), and dry ether (70 c.c.). A brisk reaction (reflux) supervened and the mixture was occasionally shaken during an hour and then warmed for a few minutes on the steam-bath. The sodium salt was separated and after acidification of its aqueous solution with acetic acid, a product, m. p. 55—56°, was isolated (8·1 g.). After crystallisation from methyl alcohol the m. p. was 57° (literature, 54·5°).

6-*Hydroxy*-5 : 7 : 4′-*trimethoxy*-4-*methylflavylium Chloride* (XXV). —A mixture of 2 : 6-dimethoxyquinol (3·4 g.), anisoylacetone (4 g.), and formic acid (50 c.c.; 98—100%) was saturated with hydrogen chloride for several hours and next day the oxonium salt was precipitated as a red, crystalline powder (5·5 g.) by the addition of ether. The *chloride* crystallised from dilute hydrochloric acid in stellar aggregates of slender, red needles (Found in material dried in a vacuum over potassium hydroxide: C, 58·4; H, 5·7. $C_{19}H_{19}O_5Cl,1·5H_2O$ requires C, 58·5; H, 5·7%). On heating, the salt lost water at 120° and then melted with decomposition at 139° to 145° according to the rate of heating. It dissolves in hot water to a red solution and in hot dilute hydrochloric acid to an orange solution. Addition of sodium carbonate to an aqueous solution gives a deep red liquid tinged with purple; on keeping, it becomes turbid and yellow. The reaction with sodium hydroxide is similar, but the change is more rapid. Sodium acetate, added to an aqueous solution, gives the pseudo-base as a dirty grey precipitate. The intensely golden-yellow solution in sulphuric acid does not exhibit fluorescence. Ferric chloride gives no characteristic reaction. After a solution of the salt in 20% aqueous potassium hydroxide had been refluxed for 1 hour (atmosphere of hydrogen), *p*-acetylanisole was isolated from the products by means of ether. The semicarbazone crystallised from alcohol in needles, m. p. 197°, alone or mixed with an authentic specimen. The *ferrichloride* crystallised from acetic acid in flat, elongated prisms, m. p. 205°, that are reddish-brown by reflected light and pale orange-brown by transmitted light (Found: C, 43·7; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·4; H, 3·7%).

5 : 7-*Dihydroxy*-6 : 4′-*dimethoxy*-4-*methylflavylium Chloride* (XXVI).—A moderately rapid stream of hydrogen chloride was passed through a mixture of iretol (1·6 g.), anisoylacetone (2 g.), and formic acid (30 c.c.; *d* 1·2) for 2 hours. The glistening, red prisms that separated (3·25 g.) crystallised from 3% hydrochloric acid (1 g. required about 400 c.c.) in shining, red needles, which became duller on being kept in a vacuum over sodium hydroxide for 3 days (Found: C, 60·0; H, 5·2. $C_{18}H_{17}O_5Cl,0·5H_2O$ requires

C, 60·4; H, 5·1%). This specimen darkened rapidly at 100—105°, was very dark at 120°, shrank at 135°, became black at 150°, and melted with vigorous decomposition at 208°. On the other hand, an air-dried specimen lost water at 120°, but the salt darkened very slowly; it blackened from 170° to 190° and melted with vigorous decomposition at 208°.

The chloride is moderately readily soluble in water and alcohol, giving bright red solutions, and is sparingly soluble in dilute hydrochloric acid, the solution being reddish-orange. The reddish-yellow solution in sulphuric acid becomes deep red on warming. Sodium carbonate, added to an aqueous solution, gives a purplish-red coloration, persistent even on boiling, but with sodium hydroxide the red colour changes to yellow and on boiling the odour of *p*-acetylanisole becomes apparent. This salt exhibits no characteristic ferric chloride reaction, a fact of interest in connexion with the constitution of carajurin.

Addition of sodium acetate to a solution of the chloride caused the separation of the red anhydro-base as an oil, which solidified and was soluble in hot benzene to a deep red solution.

The *ferrichloride* crystallised from acetic acid in compact, rhombic prisms, m. p. 180—181° with slight previous darkening (Found: C, 42·3; H, 3·5. $C_{18}H_{17}O_5Cl_4Fe$ requires C, 42·3; H, 3·4%). The crystals were red in mass, exhibited a blue metallic lustre, and appeared brown when viewed by transmitted light.

5 : 6 : 7 : 4′-*Tetramethoxy*-4-*methylflavylium Ferrichloride*.—A mixture of antiarol (2·7 g.), anisoylacetone (3 g.), and formic acid (35 c.c.; *d* 1·2) was treated with hydrogen chloride for 6 hours, and the saturated solution then kept for several days. The *chloride*, precipitated by ether (4·6 g.), crystallised from dilute hydrochloric acid in slender, silky, orange-red needles, m. p. 143—144° (decomp. and previous darkening). The *ferrichloride* crystallised from acetic acid in golden-yellow needles, m. p. 176° (Found: C, 44·5; H, 4·0. $C_{20}H_{21}O_5Cl_4Fe$ requires C, 44·5; H, 3·9%).

5 : 6 : 7 : 4′-*Tetrahydroxy*-4-*methylflavylium Chloride* (XXVII).—(A) *From the trimethyl ether* (XXV). In our earlier experiments we obtained a specimen of the demethylated chloride in the usual manner; it formed reddish-brown prisms exhibiting a bluish-green lustre (Found: C, 57·8; H, 4·7; Cl, 10·3; loss at 105—110° in a high vacuum, 2·7. $C_{16}H_{13}O_5Cl,0·5H_2O$ requires C, 58·3; H, 4·3; Cl, 10·8; H_2O, 2·7%. The monomethyl ether, $C_{17}H_{15}O_5Cl,H_2O$, requires C, 57·9; H, 4·9; Cl, 10·1; H_2O, 5·1%). It was clearly impossible to be sure that demethylation was complete and the process was therefore investigated quantitatively. A specimen of the initial material (XXV) was twice crystallised from 7[illegible]

hydrochloric acid and dried in a vacuum desiccator over sodium hydroxide; it differed somewhat from that described above and, on heating, lost water at 120° and melted at 142—143° with effervescence (Found: C, 49·9; H, 6·0%). We suspect that this product may have had the composition $C_{19}H_{19}O_5Cl,HCl,3H_2O$, which requires C, 50·3; H, 5·8%, but it was sufficient for our purpose that the analysis indicated that it contained 71·4% of the anhydro-base $C_{19}H_{18}O_5$. When the salt (0·3156 g.), mixed with phenol (8·0 g.) and hydriodic acid (20 c.c.; *d* 1·7), was heated at 135—145° in an atmosphere of carbon dioxide, demethylation was complete after 3 hours (Found: MeO, 19·8. Calc.: MeO, 20·4%), and this was confirmed in two further experiments. In the absence of phenol, however, demethylation was incomplete (Found: MeO, 17·7%). The *iodide* was isolated, after the addition of ether, in lustrous, brownish-red, diamond-shaped plates that appeared pale brown by transmitted light. Addition of hydriodic acid to its hot solution in alcohol caused the separation of characteristic, glistening, radiating clusters of flat, red needles. On heating, it began to shrink and darken at 278° and melted with decomposition at 290°. When treated with pyridine (compare the behaviour of the lower homologue carajuretin hydriodide, p. 3025), the salt dissolved, but on stirring, needle crystals, changing to prisms, separated. The anhydro-base could not be isolated in a sufficiently pure form for analysis.

The *chloride* was prepared from the iodide in alcoholic solution in the usual manner by means of silver chloride. It was twice recrystallised by the addition of concentrated hydrochloric acid to its alcoholic solution, which was then concentrated and cooled, and was obtained in reddish-brown, oblique, frequently twinned prisms. The smaller crystals appeared reddish-brown, but the larger ones had a bluish-green metallic reflex (Found in material dried in a vacuum over sodium hydroxide: C, 58·5; H, 4·5. $C_{16}H_{13}O_5Cl,0·5H_2O$ requires C, 58·3; H, 4·3%). A specimen was again crystallised (Found: C, 58·6; H, 4·4%). The salt gradually darkened above 200°, lost its lustre at about 255°, and became very dark at 270°, but did not melt at 320°. It is sparingly soluble in cold water and moderately readily soluble in hot water to a red solution. Other properties are mentioned below.

(B) *From the dimethyl ether* (XXVI). The chloride (0·3—0·4 g.) was demethylated by means of hydriodic acid (20 c.c.; *d* 1·7) in presence of phenol (8 g.) for 3 hours at 135—145° with passage of carbon dioxide. The methyl iodide was absorbed in pyridine (Found: MeO, 16·7, 16·6. Calc.: MeO, 17·3%). The isolated *iodide* had all the properties mentioned above under (A), but the

chloride, in this case very sparingly soluble in alcohol, crystallised in well-formed, hexagonal tablets, reddish-brown by transmitted light and exhibiting a splendid green lustre (Found : C, 59·9 ; H, 4·1. $C_{16}H_{13}O_5Cl$ requires C, 59·9 ; H, 4·1%). The crystals separated from a hot solution during the distillation of the alcohol and this may account for their anhydrous character, but the superficial difference between this specimen and the one obtained as above under (A) was sufficiently great to give us at first the impression that the substances were structurally different. Further experiments and comparison with the analogous case of scutellareinidin chloride have made it clear that the chlorides from (A) and (B) were, in fact, identical, although the latter was the purer specimen. The behaviour on heating was the same as that cited above (under A) and all the reactions and solubility relations of the two specimens were found to be identical. The salt is a homologue of carajuretin hydrochloride and in some of its properties resembles this substance. A solution in aqueous sodium carbonate has a brownish-cherry-red colour, but on dilution with alcohol the change of shade towards blue is not so pronounced as is the case with carajuretin. The damson solution in aqueous sodium hydroxide is not so intensely coloured as an equivalent solution of carajuretin and when it fades it becomes more brownish-yellow. The colour reaction with ferric chloride in alcoholic solution was brownish-red ; the violet tinge observed with carajuretin was absent. For purposes of comparison of the specimens prepared as under (A) and (B), the behaviour of the salt with acetone, chloroform, sodium acetate, ammonia, concentrated hydrochloric and sulphuric acids was observed, but the details need not be recorded.

5 : 6 : 7 : 4′-*Tetramethoxyflavylium Chloride* (XXVIII).—A mixture of antiarolaldehyde (4·2 g.), *p*-acetylanisole (3 g.), and acetic acid (10 c.c.) was saturated with hydrogen chloride at 60° for 6 hours ; on cooling and keeping, bright red needles were copiously deposited (6·5 g.). On heating, the salt lost water at 100—120°, darkened at 140°, and had m. p. 145—146° (decomp.). It is sparingly soluble in cold water, acetone, or dilute hydrochloric acid, more readily soluble in alcohol, and all its solutions have a golden-yellow colour. The amber-yellow solution in concentrated sulphuric acid did not fluoresce and on heating became bright red and then deep red. The *ferrichloride* crystallised from acetic acid in orange, elongated prisms, m. p. 170° (Found : C, 43·5 ; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·4 ; H, 3·7%).

5 : 6 : 7 : 4′-*Tetrahydroxyflavylium Chloride* (*Scutellareinidin Chloride, Carajuretin Hydrochloride*) (VI).—A mixture of tetramethoxyflavylium chloride (2·5 g.), phenol (8 g.), and hydriodic

acid (70 c.c.; *d* 1·7) was boiled in an atmosphere of carbon dioxide for 20—30 minutes. The salt passed into solution, but glistening, deep red crystals slowly separated again and, after cooling, these were isolated (2·2 g.). The substance decomposed from 200—270° without melting.

The iodide was converted in the usual manner into the *chloride*, which crystallised from alcohol, containing concentrated hydrochloric acid, in shining, reddish-brown plates exhibiting a green reflex (Found: C, 59·3, 59·5; H, 4·1, 4·1. $C_{16}H_{13}O_5Cl$ requires C, 59·9; H, 4·1%). As a result of later work we now regard this substance as consisting essentially of a *scutellareinidin chloride monomethyl ether*. It does not melt below 285°.

Demethylations were then effected in which the amount of methyl iodide produced was estimated. The 5 : 6 : 7 : 4′-tetramethoxyflavylium chloride employed was crystallised from 10% hydrochloric acid and obtained in hair-fine, red needles which were dried in a vacuum over sodium hydroxide. As before, the m. p. was 145—146° (decomp.), but the chlorine content (11·3%) indicated a complex constitution ($C_{19}H_{19}O_5Cl$ requires Cl, 9·8%). The theoretical methoxyl content was therefore calculated from the results of combustions (Found: C, 55·2, 55·4; H, 5·7, 5·8; and hence complete demethylation requires MeO, 30·1%). The salt (0·3038 g.) was heated at 135—145° with hydriodic acid (20 c.c.; *d* 1·7) for 2·5 hours (Found: MeO, 22·9. Calc.: for 3MeO, 22·6%); in later experiments the quantities of the salt and of hydriodic acid were similar. Addition of 2 g. of phenol raised the methoxyl eliminated to 24·6%; 6 g. raised it to 28·3%; and using 8 g. of phenol and heating for 3 hours, we found MeO, 29·5% in two experiments. The last conditions were accordingly employed in the preparation of scutellareinidin iodide, and the phenol and hydriodic acid were always heated together at 135—140° to remove impurities before the introduction of the flavylium salt. The *iodide* was collected after the addition of ether and had all the properties previously mentioned as characteristic of carajuretin hydriodide. The *chloride* crystallised from alcohol–concentrated hydrochloric acid in reddish-brown, rhombic tablets exhibiting a dark green metallic lustre (Found in material dried in a vacuum over sodium hydroxide: C, 58·6; H, 3·8. $C_{15}H_{11}O_5Cl$ requires C, 58·7; H, 3·6%). This specimen, therefore, was anhydrous, whereas carajuretin hydrochloride crystallised with $1H_2O$; nevertheless a direct comparison showed that the substances were identical, and this is a further example of the small reliance to be placed on the extent of hydration of flavylium salts as a guide to their individuality. Another case is mentioned above and it may be recalled that Malkin and

Robinson (J., 1925, **127**, 1190) obtained two specimens of pelargonidin chloride 3 : 4′-dimethyl ether, only one of which persistently crystallised in a hydrated form. All the reactions and properties given above under the heading "carajuretin hydrochloride" were also found to be characteristic of scutellareinidin chloride and a specimen of the latter having the steel-blue appearance of the former was obtained by repeated crystallisation. Finally, scutellareinidin chloride was converted into an acetyl derivative of the pseudo-base as previously described for the carajuretin derivative. The substance had m. p. 156—157°, alone or mixed with *O*-penta-acetyldihydrocarajuretinol, and the other properties of the specimens exhibited no divergences.

5 : 7-*Dihydroxy*-6 : 4′-*dimethoxyflavylium Chloride* (XI).—A solution of *p*-anisyl β-hydroxyvinyl ketone (from 4 g. of the copper derivative) in dry ether (100 c.c.) was added to one of iretol (2·2 g.) in dry ether (200 c.c.), and the mixture saturated with hydrogen chloride for 6 hours. The red solid was separated (4 g.) and extracted with very dilute hydrochloric acid; the filtered solutions deposited microscopic red crystals, which were recrystallised from 9% hydrochloric acid, only 0·18 g. of the pure salt being obtained. The salt was also obtained and in rather better yield by using dry ethyl acetate as the solvent; it crystallised in minute, red needles (Found* : MeO, 17·4. $C_{17}H_{15}O_5Cl,H_2O$ requires 2MeO, 17·6%). It did not melt at 260° and was moderately readily soluble in alcohol and in water to red solutions that gave no distinctive coloration with ferric chloride. A further distinction from carajurin hydrochloride was the solubility in aqueous sodium carbonate to a red solution.

The chloride (0·16 g.) was added to phenol (4 g.) and hydriodic acid (10 c.c.; *d* 1·7), and the mixture boiled with passage of carbon dioxide for 1·5 hours. After cooling and addition of ether, the demethylated iodide (0·13 g. of maroon needles) was collected and transformed into the chloride in the usual manner. This salt (yield, 0·08 g.) crystallised from alcohol–concentrated hydrochloric acid in clumps of dark reddish-brown, flat prisms or plates having a bluish-green reflex. On solution in 0·5% hydrochloric acid and addition of concentrated hydrochloric acid, woolly, orange-red needles were obtained and on reheating and slow cooling, glistening, rhombic prisms exhibiting a steel-blue reflex were deposited. The colour of the acid solutions, the solubility relations, and the reactions with alkalis and with ferric chloride were all identical with those of scutellareinidin chloride and carajuretin hydrochloride. The preparation of *O*-penta-acetyldihydrocarajuretinol could not be attempted in this case owing to paucity of material and the poor yield in the acetylation.

5 : 6 : 7-*Trimethoxyflavylium Salts.*—A mixture of antiarol-aldehyde (5·6 g.), acetophenone (3·2 g.), and acetic acid (10 c.c.) was saturated with hydrogen chloride at 65—70° for 6—7 hours. After keeping for 12 hours, the flavylium chloride was precipitated by the addition of ether as a reddish-brown, crystalline mass; this crystallised from 9% hydrochloric acid (100 c.c.) in slender, golden-yellow, silky needles (yield, 8·2 g.) which darkened at 110° and had m. p. 124—125° (decomp.). The salt is readily soluble in hot water, hot dilute hydrochloric acid, cold alcohol, or acetone to golden-yellow solutions. Its amber-yellow solution in sulphuric acid becomes bright red and then deep red on heating; consequently this reaction, shared with many other substances described in this communication, is due to the tetrahydroxybenzene nucleus. The cream-coloured pseudo-base is precipitated by the addition of sodium acetate or sodium carbonate to an aqueous solution of the chloride. The *ferrichloride* crystallises from acetic acid in well-formed, deep red prisms, m. p. 151°, exhibiting a bluish glance and appearing brownish-yellow by transmitted light (Found: C, 43·9; H, 3·5. $C_{18}H_{17}O_4Cl_4Fe$ requires C, 43·7; H, 3·5%). The derivative is readily soluble in acetone to a red solution.

5 : 6 : 7-*Trihydroxyflavylium Chloride* (*Baicaleinidin Chloride*) (XXIX).—5 : 6 : 7-Trimethoxyflavylium chloride (3 g.) and phenol (10 g.) were added to hydriodic acid (70 c.c.; *d* 1·7) and the mixture was gently boiled in a stream of carbon dioxide for 1 hour. In this case the salt remained in solution during the operation and we attribute the complete demethylation observed to this circumstance. After cooling, the iodide crystallised and was collected and washed with ether (yield, 1·5 g.); it formed long, transparent prisms, reddish-brown by reflected and pale brown by transmitted light. It sintered above 225° and had m. p. 254° (decomp.). The conversion into the *chloride* was carried out in dilute alcoholic solution by means of precipitated silver chloride; after concentration the salt separated in bluish-red, metallic-looking crystals (1·8 g.) and was recrystallised from 9% hydrochloric acid (500 c.c.). The glistening, dark maroon, elongated prisms with rectangular ends were dried in a vacuum over sodium hydroxide, causing them to become opaque and lustreless (Found: C, 59·6, 59·6; H, 4·0, 4·1. $C_{15}H_{11}O_4Cl,0·5H_2O$ requires C, 60·1; H, 4·0%). A specimen was boiled with hydriodic acid (*d* 1·7) and phenol for 4 hours, but no trace of methyl iodide was produced. The salt darkened above 220° and at 250—252° appeared to soften and decompose, leaving a black mass which did not melt at 320°. The chloride is sparingly soluble in water to a brownish-yellow solution and gives a reddish-brown coloration with sodium hydroxide, sodium carbonate, and

even with sodium acetate. The brownish-red alcoholic solution becomes much more intensely reddish-brown on the addition of ferric chloride.

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CCCCIII.—*The Reimer–Tiemann Reaction with* m-*Bromo- and* m-*Iodo-phenol.*

By HERBERT HENRY HODGSON and THOMAS ALFRED JENKINSON.

MIXTURES of 4-bromo-2-hydroxy- and 2-bromo-4-hydroxy-benzaldehyde and of 4-iodo-2-hydroxy- and 2-iodo-4-hydroxy-benzaldehyde in almost equal quantities have been obtained by the Reimer–Tiemann reaction from *m*-bromo- and *m*-iodo-phenol, respectively, which in this respect behave like *m*-chlorophenol (this vol., p. 1740). The individual constitutions were determined by the methods previously adopted (*loc. cit.*).

Walther and Wetzlich (*J. pr. Chem.*, 1900, **61**, 198) describe a substance of m. p. 52° as either 2- or 3-bromo-4-methoxybenzaldehyde. The latter constitution appears to be correct, since the 2-bromo-compound is now found to melt at 77°.

EXPERIMENTAL.

General.—Unless otherwise stated, the methods of preparation, general properties, and crystalline form of the various products now recorded are identical with those of the chloro-analogues (*loc. cit.*). The colours produced by alcoholic alkalis on alcoholic solutions of the *p*-nitrophenylhydrazones are given immediately after the m. p.'s.

(a) *The Reaction with* m-*Bromophenol.*

4-Bromo-2-hydroxybenzaldehyde (yield, 14 g. from 67 g. of *m*-bromophenol), on being warmed with acetic anhydride and a little sulphuric acid, gives a mixture of mono- and tri-acetates. The *sodium*, *potassium*, and *copper* derivatives have been prepared. The oxime melts at 168° (Müller, *Ber.*, 1909, **42**, 3698, gives m. p. 151°) (Found : Br, 37·1. Calc.: Br, 37·0%). The p-*nitrophenylhydrazone* crystallises in orange-yellow micro-needles, m. p. 258° (decomp.); cherry-red (Found : Br, 23·7. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%). The *semicarbazone* has m. p. 212° (Found : Br, 31·2. $C_8H_8O_2N_3Br$ requires Br, 31·0%). The *benzoate* is best prepared by gently

warming the sodium derivative (0·5 g.) with benzoyl chloride (0·3 g.), and separates from alcohol in colourless needles, m. p. 115° (Found: Br, 26·3. $C_{14}H_9O_3Br$ requires Br, 26·2%); the pyridine method of preparation (*loc. cit.*) failed.

4-*Bromo*-2-*methoxybenzaldehyde*, obtained best from 4-amino-2-methoxybenzaldehyde (*loc. cit.*), melts at 71° (Found: Br, 37·3. $C_8H_7O_2Br$ requires Br, 37·2%). *Oxime*, m. p. 132° (Found: Br, 34·8. $C_8H_8O_2NBr$ requires Br, 34·8%). p-*Nitrophenylhydrazone*, bright orange needles, m. p. 215°; violet-red (Found: N, 12·1. $C_{14}H_{12}O_3N_3Br$ requires N, 12·0%). *Semicarbazone*, m. p. 224° (Found: Br, 29·3. $C_9H_{10}O_2N_3Br$ requires Br, 29·4%). 4-*Bromo*-2-*methoxybenzoic acid*, m. p. 155° (Found: Br, 34·5. $C_8H_7O_3Br$ requires Br, 34·6%).

4-*Bromo*-2-*hydroxybenzoic acid*, colourless plates, m. p. 214° (Found: Br, 36·7. $C_7H_5O_3Br$ requires Br, 36·9%); it gives a violet colour with ferric chloride.

2-Bromo-4-hydroxybenzaldehyde (yield 15 g.; compare isomeride above) gives copper and alkali-metal derivatives. The p-*nitrophenylhydrazone* forms dark red micro-needles, m. p. 274° (decomp.); cherry-red (Found: Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%). The *semicarbazone* has m. p. 212° (Found: Br, 30·9. $C_8H_8O_2N_3Br$ requires Br, 31·0%). The oxime forms colourless needles, m. p. 184° (Gattermann, *Annalen*, 1907, **357**, 335, gives m. p. 128·5°) (Found: Br, 37·0. Calc.: Br, 37·0%).

2-Chloro-4-methoxybenzaldehyde (m. p. 62·5°. Compare Tiemann, *Ber.*, 1891, **24**, 699) and 2-*bromo*-4-*methoxybenzaldehyde*, m. p. 77° (Found: Br, 37·1. $C_8H_7O_2Br$ requires Br, 37·2%) possess hawthorn-like odours, are insoluble in water, volatile in steam, and crystallise from alcohol in long, colourless needles; the *oximes* both melt at 93° (Found: Br, 34·5. $C_8H_8O_2NBr$ requires Br, 34·8%), the p-*nitrophenylhydrazones*, orange-red needles, melt at 249° (decomp.), violet (Found: N, 13·7. Calc.: N, 13·7%), and 250° (decomp.), reddish-violet (Found: Br, 22·8. $C_{14}H_{12}O_3N_3Br$ requires Br, 22·8%), respectively; the *semicarbazones*, colourless micro-needles, melt at 240° (Found: Cl, 15·7. $C_9H_{10}O_2N_3Cl$ requires Cl, 15·6%) and 232° (Found: Br, 29·2. $C_9H_{10}O_2N_3Br$ requires Br, 29·4%). 2-*Bromo*-4-*methoxybenzoic acid*, m. p. 199° (Found: Br, 34·4. $C_8H_7O_3Br$ requires Br, 34·6%), crystallises from alcohol in short needles. 2-*Bromo*-4-*hydroxybenzoic acid* was best prepared from 3-bromo-4-nitrophenol by reduction, conversion into 3-bromo-4-cyanophenol, and hydrolysis with sulphuric acid; it crystallises from water in colourless needles, m. p. 151° (Found: Br, 36·8. $C_7H_5O_3Br$ requires Br, 36·9%), and gives a faint pink colour with ferric chloride.

(*b*) *The Reaction with* m-*Iodophenol.*

4-*Iodo*-2-*hydroxybenzaldehyde*, m. p. 87° (yield, 12 g. from 73 g. of *m*-iodophenol) is more slowly volatile in steam than its halogeno-analogues (Found: I, 51·1. $C_7H_5O_2I$ requires I, 51·2%). The *alkali-metal*, *ammonium*, and *silver* derivatives are all yellow and readily soluble in water; the green *copper* derivative is bluer than its isomeride. *Oxime*, m. p. 171° (Found: I, 48·2. $C_7H_6O_2NI$ requires I, 48·3%). p-*Nitrophenylhydrazone*, orange needles, m. p. 242° (decomp.); cherry-red (Found: I, 33·0. $C_{13}H_{10}O_3N_3I$ requires I, 33·1%). *Semicarbazone*, pale yellow needles, m. p. 252° (Found: I, 41·4. $C_8H_8O_2N_3I$ requires I, 41·6%). *Benzoate*, best prepared by the action of benzoyl chloride on the silver derivative, melts at 62° (Found: I, 36·0. $C_{14}H_9O_3I$ requires I, 36·1%).

4-*Iodo*-2-*methoxybenzaldehyde*, m. p. 85° (Found: I, 48·1. $C_8H_7O_2I$ requires I, 48·4%). *Oxime*, m. p. 138° (Found: I, 45·6. $C_8H_8O_2NI$ requires I, 45·8%). p-*Nitrophenylhydrazone*, orange-red needles, m. p. 238° (decomp.); violet-red (Found: I, 31·8. $C_{14}H_{12}O_3N_3I$ requires I, 32·0%). *Semicarbazone*, m. p. 228° (Found: I, 39·7. $C_9H_{10}O_2N_3I$ requires I, 39·8%). 4-*Iodo*-2-*methoxybenzoic acid*, m. p. 150° (Found: I, 45·9. $C_8H_7O_3I$ requires I, 45·7%), sublimes between 120° and 130° and when heated above the m. p. evolves iodine.

4-*Iodo*-2-*hydroxybenzoic acid*, colourless plates, m. p. 230° (decomp.) (Found: I, 47·8. $C_7H_5O_3I$ requires I, 48·1%); it gives a reddish-violet colour with ferric chloride.

2-*Iodo*-4-*hydroxybenzaldehyde* is odourless, non-volatile in steam, and crystallises from alcohol in very pale yellow needles, m. p. 163° (Found: I, 51·0. $C_7H_5O_2I$ requires I, 51·2%). The *alkali-metal* derivatives are yellow and the *copper* derivative is less bluish-green than its isomeride. p-*Nitrophenylhydrazone*, dark red needles, m. p. 265° (decomp.); cherry-red (Found: I, 33·0. $C_{13}H_{10}O_3N_3I$ requires I, 33·1%). *Semicarbazone*, pale yellow plates, m. p. 232° (decomp.) (Found: I, 41·3. $C_8H_8O_2N_3I$ requires I, 41·6%). *Oxime*, long, colourless needles, m. p. 155° (Found: I, 48·1. $C_7H_6O_2NI$ requires I, 48·3%). *Benzoate*, m. p. 112° (Found: I, 36·1. $C_{14}H_9O_3I$ requires I, 36·1%).

2-*Iodo*-4-*methoxybenzaldehyde* has a faint hawthorn-like odour, is volatile in steam, and crystallises from alcohol in colourless needles, m. p. 115° (Found: I, 48·5. $C_8H_7O_2I$ requires I, 48·4%). p-*Nitrophenylhydrazone*, reddish-orange needles, m. p. 247° (decomp.); reddish-violet (Found: I, 31·8. $C_{14}H_{12}O_3N_3I$ requires I, 32·0%). *Semicarbazone*, pale yellow needles, m. p. 211° (Found: I, 39·5. $C_9H_{10}O_2N_3I$ requires I, 39·8%). *Oxime*, colourless needles, m. p. 101° (Found: I, 45·6. $C_8H_8O_2NI$ requires I, 45·8%).

2-Iodo-4-methoxybenzoic acid, m. p. 184° (Found: I, 45·8. $C_8H_7O_3I$ requires I, 45·7%). *2-Iodo-4-hydroxybenzoic acid* was best prepared from 2-iodo-4-nitrotoluene; it crystallises from water (charcoal) in colourless needles, m. p. 179° (decomp.) (Found: I, 47·9. $C_7H_5O_3I$ requires I, 48·1%), and gives no colour with ferric chloride.

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CCCCIV.—*The Mechanism of the Formation of Citric and Oxalic Acids from Sugars by* Aspergillus niger. *Part II.*

By THOMAS KENNEDY WALKER, VIRA SUBRAMANIAM, and FREDERICK CHALLENGER.

THE production of citric and oxalic acids when *A. niger* is grown upon solutions containing glucose and traces of inorganic salts has been observed by many workers. In a previous communication (this vol., p. 200), it was shown that acetone, malonic acid, and glyoxylic acid can be detected in cultures of the mould on citric acid. The formation of glycollic, glyoxylic, and oxalic acids by the action of *A. niger* on calcium acetate was also established, and the suggestion was brought forward that the change glucose ⟶ citric acid ⟶ oxalic acid takes place in stages thus: glucose ⟶ gluconic acid ⟶ saccharic acid ⟶ $\beta\gamma$-diketoadipic acid ⟶ citric acid ⟶ acetonedicarboxylic acid ⟶ malonic and acetic acids ⟶ acetic acid (2 mols.) ⟶ glycollic acid ⟶ glyoxylic acid ⟶ oxalic acid.

Molliard, Butkewitsch, and Bernhauer have shown that gluconic acid is readily produced in cultures of *A. niger* on glucose, while both Wehmer and Schreyer have converted gluconic acid into citric acid by the further action of this or a similar mould. The present authors (*loc. cit.*) brought forward strong evidence of the formation of citric acid when *A. niger* is grown on solutions of dipotassium saccharate. It was detected by the formation of the basic mercuric sulphate compound of mercuric acetonedicarboxylate on treatment of the culture with acidified mercuric sulphate and potassium permanganate (Denigès' test, *Ann. Chim. Phys.*, 1899, **18**, 414). The citric acid was characterised as dibenzylideneacetone.

The statement of Broeksmit (*Pharm. Weekblad*, 1917, **54**, 687)

that oxidation of malic acid by potassium permanganate gives rise to acetone, detected solely by formation of iodoform with iodine and ammonium iodide, would, if correct, render identification of citric acid by this method uncertain. It is difficult to see how malic acid could yield acetone on oxidation, and on repeating Broeksmit's test a strong odour of acetaldehyde was noticed. Acetaldehyde readily gives iodoform with iodine in ammonium iodide, such a solution being no specific test for acetone.

In the case of the cultures on dipotassium saccharate it was not possible to separate the citrate as calcium salt from the large excess of saccharate (see p. 3049). Evidence of the production of acetonedicarboxylic acid (ferric chloride test) on oxidation of the contents of the culture medium was, however, obtained. When the mould is grown on potassium hydrogen saccharate solution, potassium citrate is formed in considerable amount. Further evidence of the importance of saccharic acid in the mycological production of citric acid is afforded by its isolation in the form of the potassium hydrogen salt from cultures of *A. niger* on glucose. Apart from the observation of Grüss (*Jahrbuch. wiss. Bot.*, 1926, **66**, 155, 171, 177) that saccharic acid is formed by the action of the nectar yeasts *Anthomyces Reukaufii* and *Amphiernia rubra* on glucose, this would appear to be the only recorded instance of the production of this acid by micro-organisms. Grüss identified it microscopically as the cæsium hydrogen salt.

In cultures of the nectar yeast *Microanthomyces septentrionalis* on glucose Grüss found gluconic and oxalic acids (*Woch. Brauerei*, 1927, **44**, 233).

In view of the occurrence of gluconic acid in *A. niger* cultures, and of the results just mentioned, it was to be expected that gluconic acid would yield saccharic acid by the action of the mould. This has been shown to be the case, since growth of *A. niger* on calcium gluconate solutions gives rise to calcium saccharate and some citrate. A different type of reaction was observed by Boutroux (*Compt. rend.*, 1886, **102**, 924) and by Bertrand (*Ann. Chim. Phys.*, 1904, **3**, 279), who isolated δ-ketogluconic acid from cultures of a micrococcus and of the sorbose bacteria on gluconic acid or its calcium salt. The same result was obtained by Kluyver and de Leuuw (*Tijdschrift voor vergelykende geneeskunde*, 1924, No. 10) with *Acetobacter suboxydans* and calcium gluconate.

Seekamp (*Annalen*, 1893, **278**, 374) describes the photochemical formation of acetone from aqueous citric acid in presence of uranium oxide. In Part I of this research the formation of acetone in cultures of *A. niger* on citric acid was demonstrated and ascribed to the decarboxylation of acetonedicarboxylic acid, although proof

of its presence was lacking. By employing ammonium citrate instead of the free acid, acetonedicarboxylic acid has now been detected by the colour test with ferric chloride, and by the formation of the diphenylhydrazone of mesoxaldialdehyde on treatment of the culture with benzenediazonium chloride (von Pechmann and Jenisch, *Ber.*, 1891, **24**, 3257).

The only reference in the literature to the possible formation of this acid by a micro-organism is afforded by the observation of von Lippmann (*Ber.*, 1893, **26**, 3058; 1908, **41**, 3981) that a specimen of the calcium oxide compound of sucrose, after long keeping in a closed vessel, was converted into calcium acetonedicarboxylate. A five years old preparation had completely decomposed, giving calcium formate, acetate, oxalate and carbonate. No bacteriological examination of the products was made, but Lafar ("Handbuch der techn. Mykologie," Jena, 1908, II, 487) suggests that micro-organisms were responsible. Von Lippmann (*Ber.*, 1920, **53**, 2070) also describes the isolation of calcium malonate and calcium succinate from a solution of pure sucrose containing lime water which had become infected with bacteria, moulds, and yeasts. These observations are of interest, since malonic and acetonedicarboxylic acids have now been detected in pure cultures of *A. niger* on citric acid or a citrate. The close relations of saccharic, citric and acetonedicarboxylic acids and acetone disclosed in this research may have some bearing on the work of Wirth (*Biochem. Z.*, 1911, **33**, 49), who found that addition of gluconic, saccharic or mucic acid to blood supplied to a perfused dog's liver can lead to a decided formation of acetoacetic acid.

Oxalic acid is produced by the growth of the mould on ammonium acetonedicarboxylate, presumably by way of malonic and acetic acids, though its formation by the oxidation of "nascent" acetone produced by hydrolysis and decarboxylation is not excluded.

The tentative explanation of the mycological decomposition of citric acid suggested on p. 3044 requires the production of two molecules of acetic acid. This has not previously been detected with certainty in cultures of *A. niger* on sugars or citric acid, apart from the work of Heinze (*Ann. mycologici*, 1903, **1**, 350). This author refers to its formation in old cultures on glucose, but gives no experimental details. Acetic acid, however, may readily be isolated from ten-day cultures on citric acid, converted into acetone by dry distillation of its calcium salt, and characterised as the *p*-nitrophenylhydrazone. *B. lactis aerogenes* is stated to give rise to two equivalents of acetic acid from one of citrate (Bosworth and Prucha, *J. Biol. Chem.*, 1911, **8**, 479).

In Part I the detection of glyoxylic acid in cultures of *A. niger* on

malonic acid was described. The quantity was, however, very small, judged from the amount of the aminoguanidine derivative of glyoxylic acid which was isolated. This observation has now been confirmed, the aldehydo-acid being precipitated as the di-xanthylhydrazone (Fosse and Hieulle, *Compt. rend.*, 1925, **181**, 286), but again in very small quantity. In view of the labile nature of glyoxylic acid and its ready conversion into oxalic acid, this is perhaps not surprising. The isolation of glycollic acid from cultures of *A. niger* on calcium acetate is described in Part I. When the mould is grown upon calcium glycollate and ammonium glycollate the formation of glyoxylic and oxalic acids, respectively, may be detected, thus affording further evidence that the acetic —→ oxalic change proceeds as indicated in the scheme on p. 3044.

In Part I (this vol., 200) attention was directed to the suggestion of Franzen and Schmitt (*Ber.*, 1925, **58**, 222) that citric acid in plants is formed from saccharic acid by loss of $2H_2O$ giving rise to $CO_2H{\cdot}CH{:}C(OH){\cdot}C(OH){:}CH{\cdot}CO_2H$, which, in its keto-form, undergoes a "benzilic acid transformation," giving citric acid. The conversion of saccharic into citric acid by *A. niger* doubtless follows the same course, and is being investigated from this point of view by the authors.

Such an elimination of water from saccharic acid may possibly proceed in living organisms in a different but equally symmetrical manner, giving rise to $CO_2H{\cdot}C(OH){:}CH{\cdot}CH{:}C(OH){\cdot}CO_2H$, which by loss of carbon dioxide would yield succindialdehyde. In presence of ammonia this would form the pyrrole ring, so frequently occurring in nature. The observations of von Lippmann and of Ciskiewicz (*Ber.*, 1892, **25**, 3218; 1893, **26**, 3063) that solutions of ammonium mucate and saccharate, after spontaneous infection by atmospheric organisms, contain pyrrole are therefore of considerable interest and will be further investigated.

In view of the authors' demonstration of the biochemical significance of saccharic and acetonedicarboxylic acids, the ingredients of Robinson's synthesis of tropinone (J., 1917, **111**, 762) are seen to bear a simple relation to glucose, and the probability that similar syntheses of nitrogen compounds occur in nature (Robinson, *ibid.*, p. 880) appears to be enhanced.

Experimental.

Fermentation of Glucose. Detection of Saccharic Acid.—A medium containing glucose (300 g.), ammonium nitrate (3·2 g.), potassium dihydrogen phosphate (0·6 g.), and water (2000 c.c.) was sterilised and inoculated with a young culture of *A. niger* grown on the same

medium. A thick growth formed in 3 days at 31°. No saccharic, citric, or oxalic acid could be detected on the fourth or fifth day. On the sixth, while citric and oxalic acids were still absent, neutralisation of 150 c.c. of the culture with potassium carbonate, acidification with acetic acid, evaporation, and extraction with hot alcohol to remove glucose left a residue of about 0·2 g. of a salt giving the reactions of potassium hydrogen saccharate. Next day, traces of citric acid were detected by Denigès' test, but no oxalic acid. The whole of the solution was then neutralised and treated as before, giving 1·65 g. of a salt insoluble in alcohol, but containing much citrate. The conversion of saccharic into citric acid appears, therefore, to be very rapid after a certain phase in the development of the mould is reached. By a modification of the conditions, however, this difficulty was evaded. Twelve 300 c.c. flasks (A—L), each containing 150 c.c. of the medium, were sterilised. Six of these (A—F) were inoculated on the same day, and the remainder (G—L) after 24 hours. All were incubated at 30—32°. Growth occurred 3 days after inoculation.

Flask A was examined for saccharic, citric, and oxalic acids on the third day, flask B on the fourth day, C on the fifth, and so on. Traces of an insoluble potassium salt were isolated from C, 0·3 g. from D, and 0·8 g. from E, whilst only in E was any citric or oxalic acid to be found. After this satisfactory indication, the contents of flasks G—L were united on the sixth day after inoculation, filtered, treated with potassium carbonate and acetic acid as before, and evaporated. Repeated extraction of the residual syrup with boiling alcohol left a residue of 3·6 g. of a potassium salt. On recrystallisation from a very little hot water, this gave pure potassium hydrogen saccharate (Found: K, 15·7. Calc.: K, 15·7%. 0·0502 and 0·0461 required 20·2 and 18·5 c.c. of N/100-NaOH. Calc., 20·23, 18·57). A portion was converted into the sparingly soluble thallous hydrogen salt, and the thallium determined as thallous iodide (Found: Tl, 49·3. Calc.: Tl, 49·4%).

Fermentation of Calcium Gluconate. Detection of Saccharic Acid.—The calcium gluconate was prepared by Bert's modification of Blanchetière's method (*Bull. Soc. chim.*, 1923, **33**, 345, 733), and its purity checked by determinations of calcium (Found: Ca, 9·3. Calc.: Ca, 9·3%) and the specific rotation, $[\alpha]_D$ + 7·7°. The medium contained water (1000 c.c.), calcium gluconate (20 g.), and the usual mineral salts in the proportions contained in Molliard's solution M (this vol., pp. 202—204). Inoculation with mycelium from a 200 c.c. culture gave growths on the fourth day at 31°. On the next day the solution was filtered, concentrated to 800 c.c. under diminished pressure, and boiled; a precipitate containing calcium

citrate (1·2 g.) then separated. Further boiling produced no deposit and the filtrate was concentrated in a vacuum to 350 c.c. On cooling, a white solid (3·7 g.) separated which was free from citrate. It was recrystallised twice with difficulty from much hot water (calcium saccharate is sparingly soluble) and dried over sulphuric acid (Found : Ca, 16·0. Calc. : Ca, 16·1%).

0·7 G. was boiled with 0·5 g. of potassium carbonate in 10 c.c. of water, and the filtrate acidified with acetic acid. The resulting potassium hydrogen saccharate was recrystallised twice from hot water (0·0623 and 0·0712 required 25·0 and 28·7 c.c. of $N/100$-NaOH. Calc., 25·13, 28·8), and a portion of it then converted into thallous hydrogen saccharate (Found : Tl, 49·3. Calc. : Tl, 49·4%).

Fermentation of Dipotassium Saccharate. Detection of Citric Acid.—A solution containing 40 g. of the normal potassium salt in 2000 c.c. of solution M was sterilised and inoculated. After 28 days at 31° the presence of citric acid was detected by Denigès' test. 5 G. of the evaporated culture were oxidised by hot 2% potassium permanganate solution in presence of acidified mercuric sulphate solution, giving a white solid. A few grams of this were washed, suspended in water, and treated with hydrogen sulphide. The filtrate from the mercury sulphide was repeatedly extracted with ether, and the wet solvent evaporated under diminished pressure. The slight aqueous residue gave a reddish-purple coloration with ferric chloride, similar to that produced by acetonedicarboxylic acid, thus confirming the presence of a citrate (Denigès, *Ann. Chim. Phys.*, 1899, **18**, 408, 414). This reaction was not due to the presence of the keto-acid in the original culture, as this would have been decomposed during evaporation. Only a trace of a precipitate was obtained with mercuric sulphate before oxidation with permanganate, and this was removed.

Attempts were then made to precipitate calcium citrate from the culture, but the presence of the saccharate had a disturbing effect. Normal calcium saccharate is very sparingly soluble in water, but soluble in excess of calcium chloride. This solution gives no precipitate on boiling, even on evaporation to a small bulk. When citrate is present, however, the clear solution gives a precipitate when boiled which contains saccharate and citrate, no separation being effected. When a mixture of dipotassium saccharate and potassium citrate is treated in the cold with calcium chloride approximately equivalent to the saccharate, the resulting precipitate contains both saccharate and citrate. The filtrate on boiling deposits calcium saccharate.

When insufficient calcium chloride is added the initial precipitate of calcium saccharate redissolves. On boiling the clear solution

successive deposits are obtained which contain saccharate, citrate being present in some cases.

In other experiments, the saccharic acid was partly removed as the potassium hydrogen salt by addition of acetic acid to the concentrated culture, and the filtrate was neutralised with potassium carbonate, treated with calcium chloride, and boiled. Calcium citrate was not precipitated and it was then found that excess of sodium acetate greatly retards the precipitation of this salt from hot solutions. The effect of salts of other organic acids on the precipitation of calcium citrate appears to have received very little attention.

Fermentation of Potassium Hydrogen Saccharate. Detection and Isolation of Citric Acid.—The mould grew more readily on solutions of the potassium hydrogen salt than on those of the normal salt. A mixture of solution M (2000 c.c.) and potassium hydrogen saccharate (40 g.) was sterilised, inoculated and incubated at 31°. On the fourteenth day citric acid was detected by Denigès' reagent (*loc. cit.*, p. 384), whereupon the remainder of the solution (1800 c.c.) was filtered, concentrated under diminished pressure, and evaporated, leaving 36 g. of moist residue. A duplicate experiment yielded 34 g. The residues were united and heated under reflux for 1 hour with 400 c.c. of 65% alcohol (in which potassium hydrogen saccharate is insoluble, but potassium citrate is easily soluble), and the solution was filtered and evaporated. The residue was converted into the lead salt, which was decomposed by hydrogen sulphide, and the filtrate from the lead sulphide was decolorised with charcoal and evaporated (3·6 g.). After three crystallisations from dry ether–light petroleum, its m. p., alone or in admixture with anhydrous citric acid (m. p. 153°), was 153·5° (0·1212 and 0·0560 required 37·7 and 17·5 c.c. of *N*/20-NaOH. Calc., 37·8, 17·5. Found: C, 37·5; H, 4·7. Calc.: C, 37·5; H, 4·2%). A portion was neutralised with potassium hydroxide and treated with thallous nitrate, and the resulting thallium salt was twice crystallised from hot water and analysed (Found: Tl, 76·4, 76·6. Calc.: Tl, 76·4%).

Fermentation of Ammonium Citrate. Detection of Acetonedicarboxylic Acid.—A medium containing ammonium citrate (20 g.) and citric acid (4 g.) in solution M (2000 c.c.) was inoculated from test-tube cultures, growth occurring on the third day at 31°. On the third, fourth, and fifth days 50 c.c. of the culture were removed, filtered, and treated with 3 g. of sodium acetate, and a benzenediazonium chloride solution (prepared from 0·3 g. of aniline) was added at 0°. On the fifth day, a red coloration was observed after 3 hours. A further 10 c.c. of the culture were shaken with 50 c.c. of cold Denigès' mercuric sulphate solution, a white precipitate being

obtained. (Acetone in dilute solution gives a precipitate only on warming.) These two tests were regarded as indications of the probable presence of acetonedicarboxylic acid.

At this stage 1800 c.c. of the filtered culture were treated with corresponding proportions of benzenediazonium chloride solution and sodium acetate at 0°. A red precipitate formed in 8 hours. This was separated, washed with ice-water, dried (1·3 g.), washed with light petroleum, and recrystallised from alcohol and then from ethyl acetate; it then melted at 175°, and at 175—176° in admixture with the diphenylhydrazone of mesoxaldialdehyde (m. p. 175—176°) prepared from acetonedicarboxylic acid and benzenediazonium chloride (Found: N, 21·3. Calc.: N, 21·1%). Both specimens gave a deep violet coloration with sulphuric acid (Bülow reaction).

Fermentation of Citric Acid. Detection of Acetic Acid.—The medium employed contained 3·5 g. of citric acid in 4000 c.c. of solution M. After sterilisation it was inoculated with 700 c.c. of a three days' culture of *A. niger* on the same medium. Growth was observed on the third day at 31°. 50 C.c. of the culture were then withdrawn on successive days and carefully distilled in steam and the volatile acids were determined. On the third and fourth days, 0·4 c.c. of *N*/20-sodium hydroxide was required, on the seventh 3·8 c.c., ninth 10·2, tenth 11·8, eleventh 11·9, twelfth 11·0. The whole of the culture was then filtered, neutralised with sodium carbonate, concentrated in a vacuum to 100 c.c., acidified with phosphoric acid, and carefully distilled in steam till the distillate was no longer acid (200 c.c.). This was neutralised with sodium carbonate and evaporated and the residue (2·8 g.) was extracted with 15 c.c. of 95% alcohol, in which sodium acetate is soluble. The residue (0·4 g.) contained no formate. The alcoholic extract was evaporated; the residue, which appeared to be sodium acetate, was converted into the silver salt, which was crystallised twice from hot water and dried (Found: Ag, 64·4, 64·8. Calc.: Ag, 64·7%). A further portion of the sodium salt was distilled with phosphoric acid, the distillate neutralised with calcium carbonate, and the dry calcium salt distilled, giving a few drops of liquid, which were warmed with 30 c.c. of Denigès' mercuric sulphate solution (Part I, p. 206). The resulting precipitate (2·8 g.) was separated and decomposed by distillation with 5 g. of sodium iodide and 10 c.c. of water, and the distillate was collected in a solution of *p*-nitrophenylhydrazine acetate (Part I, p. 207). Long, yellow needles separated in 3 hours which, recrystallised from alcohol, melted at 148·5° and did not depress the m. p. (148·5°) of an authentic specimen of acetone-*p*-nitrophenylhydrazone.

Malonic acid also is a product of the fermentation of citric acid

by *A. niger*. In order to exclude the possibility that the acetic acid arose by the decarboxylation of this acid (normally occurring at 140°) a mixture of 100 c.c. of solution M, 1 g. of citric acid, and 1 g. of malonic acid was distilled in steam. The distillate was not acid.

Fermentation of Ammonium Acetonedicarboxylate. Detection of Oxalic Acid.—The medium contained the ammonium salt (20 g.) in solution M (2000 c.c.). It was prepared and sterilised as in the case of the ammonium glycollate solution, inoculated, and incubated at 32°. Oxalate was found on the eighteenth day by removing 20 c.c., boiling with dilute hydrochloric acid to decompose the keto-acid (which gives a sparingly soluble calcium salt), neutralising the solution with ammonia, and adding calcium chloride.

The main bulk was then treated in a similar manner, complete decomposition of the keto-acid being indicated by the absence of a precipitate with Denigès' solution, which detects 1 part of acetonedicarboxylic acid in 5000 parts of water. The calcium oxalate was dissolved in hydrochloric acid, reprecipitated, and dried (1·6 g.) (Found: Ca, 31·2. Calc.: Ca, 31·25%. 0·1436 required 44·9 c.c. of $N/20$-$KMnO_4$. Calc., 44·87).

Fermentation of Malonic Acid. Detection of Glyoxylic Acid.—The medium contained 20 g. of malonic acid in 2000 c.c. of solution M. It was inoculated with mycelium from a smaller culture on the same medium and incubated at 31°. On the seventeenth day a positive reaction for glyoxylic acid was obtained with naphtharesorcinol. 1000 C.c. of the filtered culture were treated with 1 c.c. of 50% hydrazine hydrate and then with 4 g. of xanthhydrol dissolved in 1000 c.c. of glacial acetic acid. After addition of water and shaking, the precipitate was separated, and centrifuged with a slight excess of alcoholic N-sodium hydroxide; by this means any trixanthylhydrazine remains insoluble. The clear liquid was decanted and treated with acetic acid, and the pale pink crystalline precipitate was recrystallised twice from chloroform–light petroleum (0·5 g.). After drying in a vacuum over calcium chloride, it melted at 146·5°. In admixture with an authentic specimen of the dixanthylhydrazone of glyoxylic acid (m. p. 147°) it melted at 146·5°.

A blank experiment was carried out on the unfermented medium, but no precipitate was obtained on acidification of the alkaline alcoholic extract.

Fermentation of Malonic Acid. Detection of Oxalic Acid.—A sterilised solution containing 25 g. of malonic acid in 2500 c.c. of solution M was inoculated and incubated at 30°. On the eighteenth day oxalate was detected on addition of calcium chloride to the cold solution, whereupon 800 c.c. were withdrawn, filtered, concentrated

in a vacuum to 400 c.c., and neutralised with ammonia, and excess of 10% calcium chloride solution was added. The precipitate was redissolved in dilute hydrochloric acid and reprecipitated with ammonia (Found : Ca, 31·3, 31·2. Calc. : Ca, 31·25%. 0·0832 and 0·0976 required 25·9 and 30·10 c.c. of $N/20$-$KMnO_4$. Calc., 26·0, 30·5). (Under the experimental conditions any glyoxylic acid would be partly converted into oxalic acid.)

Glyoxylic acid or its ammonium salt in 2% aqueous solution gives no precipitate with cold calcium chloride unless the solution has been boiled and again cooled, calcium oxalate then being precipitated.

Fermentation of Calcium Glycollate. Detection of Glyoxylic Acid.— The medium contained 40 g. of calcium glycollate in 4000 c.c. of solution M. The water was first sterilised and the glycollate added. The solution gave no test for glyoxylic acid and was inoculated with mycelium from four test-tube cultures on the same medium and incubated at 22°. On the sixth day a mixture of 10 c.c. of the medium, 10 c.c. of hydrochloric acid, and a trace of 1 : 3-dihydroxynaphthalene was boiled for 1 minute, cooled to 16°, and extracted with ether, which acquired a purple colour (naphtharesorcinol test) indicating the presence of glyoxylic acid or a similar compound.

On the twenty-seventh day 1800 c.c. of the culture were treated with 7 g. of aminoguanidine acetate, giving after 3 days a yellow deposit (0·3 g.). On recrystallisation from hot water this had m. p. 155° and did not depress the m. p. (155°) of an authentic specimen of the aminoguanidine derivative of glyoxylic acid.

A further 1800 c.c. of the filtered medium were treated with 1 c.c. of 50% hydrazine hydrate and then with 4 g. of xanthhydrol in 1800 c.c. of glacial acetic acid (a blank experiment was carried out on 1800 c.c. of acetic acid) (see p. 3052). On addition of water a white precipitate was produced. This was separated after an hour, dried, and treated with alcoholic N-sodium hydroxide. The resulting solution was filtered and acidified with acetic acid, and the precipitate was washed with aqueous alcohol, dried over soda-lime, and twice crystallised from chloroform–light petroleum; it then melted at 147° and did not depress the m. p. (147°) of an authentic specimen of the dixanthylhydrazone of glyoxylic acid (Found: C, 71·8; H, 4·85. Calc. : C, 72·1; H, 4·7%). The acetic acid used as solvent was shown to be free from glyoxylic acid both by the naphtharesorcinol and by the xanthhydrol test.

Fermentation of Ammonium Glycollate. Detection of Oxalic Acid.— The medium contained 20 g. of ammonium glycollate in 2000 c.c. of solution M. It was not sterilised in the usual manner, the glycollic acid being dissolved in sterile water, almost neutralised with am-

monia and diluted with sterile water. Inoculation was effected with 200 c.c. of a smaller culture on the same medium. On the tenth day 1800 c.c. of the culture were filtered, treated with a slight excess of 10% calcium chloride solution, warmed, and filtered. The precipitate was dissolved in hydrochloric acid and reprecipitated with ammonia (2·9 g.) (Found: Ca, 31·2. Calc.: Ca, 31·25%. 0·1237 required 38·6 c.c. of $N/20$-$KMnO_4$. Calc., 38·65).

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CCCCV.—*The Influence of Alkalis on the Coagulation of Silica and Clay Suspensions by Alkali Chlorides.*

By HENRY BOWEN OAKLEY.

MANY studies have been made on the coagulation of clay suspensions and silicic acid sols by electrolytes, but hardly any systematic observations have been made on the influence of the reaction of the medium on the results, although Bradfield (*J. Amer. Chem. Soc.*, 1923, **45**, 1243) has shown that this factor has a great influence on the coagulation of clay, as on most other aqueous colloidal systems.

In continuance of the comparison of the properties of clay and silica made in these laboratories, a comparative study of the coagulation of a fine suspension of the latter substance was also made. The results suggested that silica on which small quantities of alumina had been precipitated might behave like clay in its coagulation by mixtures of alkali-metal chlorides and hydroxides. This proved to be the case when certain conditions were observed, and the general results lend further support to the view that the reactions involved in the absorption of alkalis by clay and its coagulation are of a chemical nature. The experiments recorded in this paper are confined to the alkali-metal and calcium chlorides and hydroxides.

Description and Preparation of Clay.—The clay used in these

experiments was No. 10195, prepared from a heavy cotton soil by decantation from 0·05% sodium carbonate. It was flocculated by dilute hydrochloric acid (N/100) and purified to a high resistance by dialysis. The molecular ratio $SiO_2 : Al_2O_3$ was about 4. The clay was practically identical with No. 6640 described by Joseph and Hancock (J., 1924, **125**, 1888) and contained 0·15% of humus. It may be objected that the process of purification may largely alter the characteristics of clay; this is certainly true in that an "acid" clay has very different properties from the same clay combined with a base, but there is no evidence that the process of purification alters the clay in any other way.

Experimental.

The Nephelometric Method of Measuring the Concentration of Clay Suspensions.—In some of the experiments the amount of clay remaining in suspension in the various tubes after 1 hour was estimated by comparison with a standard suspension of clay in a Klett nephelometer. Preliminary experiments showed that, contrary to expectation, neutral flocculants even in excess did not affect the turbidity if the suspension was stirred immediately before the measurement was made. The addition of alkalis, however, produced a very marked decrease in turbidity, the effect apparently being dependent only on the nature of the alkali and not on its concentration. The following table shows the effect produced by hydroxides and carbonates, the turbidity of a 0·1% purified clay suspension being taken as unity and used as standard.

	Ba.	Ca.	NH_4.	K.	Na.	Li.
Hydroxide	0·95	0·93	0·84	0·81	0·58	—
Carbonate	—	—	0·82	0·84	0·64	0·50

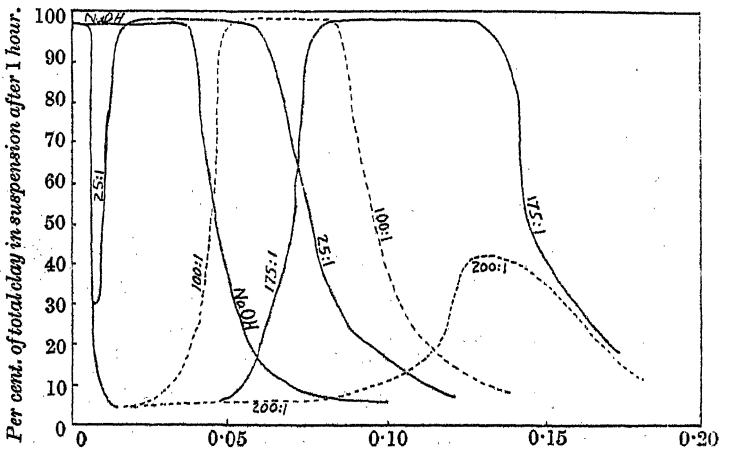
The order is approximately that of the Hofmeister series. This decrease in turbidity was allowed for in measuring the concentration of alkaline suspensions by using an alkaline standard.

The Flocculation of Clay by Mixtures of the Chlorides and Hydroxides of the Alkali Metals.—Following Bradfield (*loc. cit.*), a series of mixtures was prepared, N with respect to sodium, containing sodium chloride and sodium hydroxide in ratios ranging from 2 : 1 to 200 : 1. Each mixture was added in increasing amounts to a series of large boiling-tubes. Water was added to make the volume up to 45 c.c., and then 5 c.c. of a 1% suspension of purified clay (10195) were added at 5-minute intervals to each tube. These were shaken a dozen times by hand, and after standing undisturbed for 1 hour, 10 c.c. were withdrawn with a pipette 3·5 cm. below the surface. The height of each column of liquid was about 7 cm.

The amounts of clay in these samples were estimated in the nephelometer, and when required, the p_H of a further sample was also measured electrometrically with a Clark's cell.

Some of the results are plotted in Fig. 1. The ordinates represent the percentage of the total amount of clay remaining in suspension after 1 hour and the abscissæ the total concentration of the sodium. The interesting effect is observed that the curves for mixtures in which the ratio of chloride to hydroxide is 25 to 1 or more show a pronounced maximum and minimum, the range of the latter increasing with increasing ratio of chloride to hydroxide, until with pure sodium chloride the maximum has disappeared completely. This

FIG. 1.

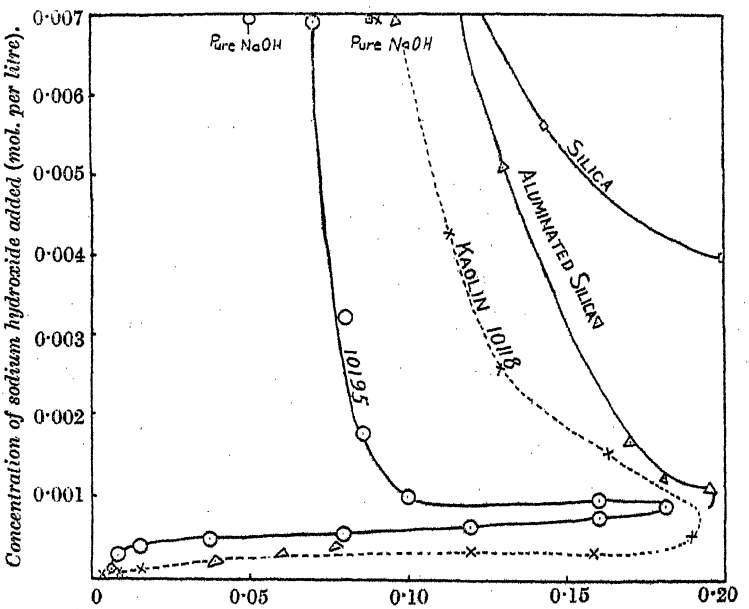


phenomenon has been observed with different clays and only fails when the initial reaction of the suspension is alkaline (*Nature*, 1926, **117**, 624). It is also shown with a more limited range of mixtures by kaolin, but here the ratio of chloride to hydroxide must not be less than 250 to 1. The same phenomenon is shown with lithium, potassium, and also calcium at much lower concentrations and for mixtures in which the ratio of calcium chloride to calcium hydroxide varies from 1 : 1 to 3 : 1.

The following scheme compares the effects of mixtures of potassium, sodium, and lithium chlorides with their respective hydroxides in which the ratio of chloride to hydroxide is 100 : 1. A minus sign indicates no flocculation in 1 hour, and a plus sign indicates that less than 30% remains in suspension after 1 hour.

Conc. of metal, × 10^3.	K.	Na.	Li.	Ca (conc. × 10^4). $CaCl_2 : Ca(OH)_2 = 2 : 1$.
2	−	−	−	−
3	+	−	−	−
5	+	−	−	−
7	+	+	−	−
10	+	+	+	−
20	+	+	+	−
30	+	+	+	−
40	±	−	−	−
50	−	−	−	−
60	−	−	−	−
80	+	−	−	+
100	+	±	−	+
140	+	+	−	−
180	+	+	+	−
200	+	+	+	+

FIG. 2.

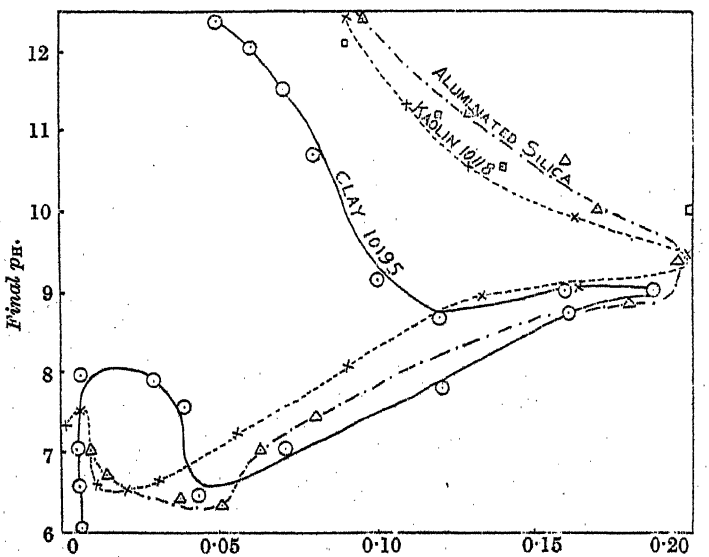


Minimal concentration of sodium (equiv. per litre) for flocculation in 1 hour.

It will be noticed that the flocculating power and the first zone of coagulation decrease in passing from potassium to lithium. This phenomenon was not observed by Bradfield (*loc. cit.*), who worked on the finest fraction of clay separated by means of a supercentrifuge. His suspension, although acid, had not been treated with *N*/100-hydrochloric acid before purification, as in the present work, and his observations were made after the suspensions had been standing for 24 hours.

The influence of the alkalinity on the minimal concentration of kation required to flocculate clay in 1 hour can best be summarised by plotting these quantities. In Fig. 2, the concentration of hydroxide added is plotted against this minimal concentration, and in Fig. 3 the final p_H is similarly plotted. The minimal concentration is defined, for the purpose of these curves, as that concentration which allows between 20 and 40% of the clay to remain in suspension after 1 hour. The results for kaolin and for silica on which a small quantity of aluminium hydroxide has been precipitated are also included in these diagrams, and will be discussed later. The most

FIG. 3.

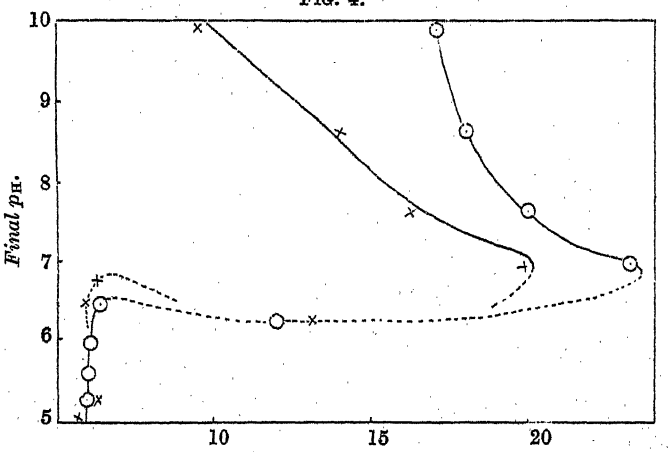


Minimal concentration of sodium (equiv. per litre) for flocculation in 1 hour. Squares represent silica.

important characteristic of these curves is that the minimal concentration of sodium required for flocculation rises very rapidly on the addition of small quantities of alkali, and reaches a very pronounced maximum when the concentration of alkali added is 0·009*N* or when the p_H is 9. This for a 0·1% suspension corresponds to the amount of sodium this clay can absorb without beginning to break down into soluble silicates and aluminates (Oakley, this vol., p. 2819). A curious feature of the curves in Fig. 3 is the sudden drop in the p_H and its subsequent rise with increasing concentrations of sodium, and this in spite of the steadily increasing concentrations of alkali as shown in Fig. 2. Although the measurements in this

neighbourhood are admittedly difficult to repeat, there is no doubt of the reality of the effect which has been observed in each of the three substances studied. The fall in p_H is due to increased absorption of sodium with increasing sodium-ion concentration accompanied by the liberation of an equivalent quantity of hydrogen ions. The combination of the clay with sodium is accompanied by an increase in the concentration of sodium ions required to flocculate it in a given time. That sodium chloride has a very large effect in decreasing the p_H of clay suspensions is shown by the following figures. The effect is far greater than that produced on sodium silicate which is in true solution, and it is generally agreed that this is due to the

FIG. 4.



Added concentration of calcium required for flocculation in 1 hour (equiv. per litre $\times 10^4$*) (circles). Specific conductance* ($\times 10^5$) *at 20° (crosses).*

combination of sodium with the clay acid, with the liberation of an equivalent quantity of free acid.

The lowering of p_H by the addition of neutral salt.

1% Clay suspension.		Sodium silicate ($SiO_2 = 0{\cdot}02M$).	
No NaCl.	$N/2$-NaCl.	No NaCl.	$N/2$-NaCl.
10·70	9·30	10·72	10·39
10·01	7·85	9·90	9·62
9·40	7·00	9·40	9·00
8·60	6·30	—	—

The Flocculation of Clay by Calcium Chloride and Hydroxide.—These results are plotted in Fig. 4; as with sodium, the minimal concentration of calcium required for flocculation shows a sudden increase to a maximum with the addition of small quantities of calcium hydroxide, but here the concentrations are about 1/10 of

those for sodium, and the p_H at the maximum is 7 instead of 9. The curve for the specific conductivity shows that the decrease in the minimal concentration above a p_H of 7 is even more marked than that indicated by the other curve, which shows the initial concentration of calcium added. As with sodium, the results indicate that the combination of the clay with calcium in the initial stages is accompanied by an increase in the concentration of calcium ions required to flocculate it in 1 hour. This is directly opposite to the results obtained by Comber (*J. Agric. Sci.*, 1920, **10**, 425) and confirmed by Kermack and Williamson (*Nature*, 1926, **117**, 824), who found that clay was more readily flocculated by calcium in an alkaline medium. The discrepancy is due to the fact that these workers used more concentrated solutions and consequently much higher rates of flocculation than those described in this paper. This is clearly shown by the following results (*Nature*, 1926, **118**, 661) for the time required to flocculate a 0·1% suspension in solutions of calcium hydroxide and chloride at various concentrations.

	Time required for flocculation.		
Conc. of $Ca^{\cdot\cdot}$ ions.	$Ca(OH)_2$.	$CaCl_2$.	$2Ca(OH)_2 + CaCl_2$.
0·001	7 hours	14 mins.	6 hours
0·002	28 mins.	10 ,,	32 mins.
0·003	2 ,,	7 ,,	12 ,,
0·004	1·5 ,,	6 ,,	4·5 ,,
0·005	1·5 ,,	6 ,,	3·5 ,,
0·010	1·5 ,,	6 ,,	1·5 ,,
0·014	1·5 ,,	6 ,,	1·5 ,,

It is shown below that a suspension of silica is only coagulated by calcium chloride or sodium chloride in an *alkaline* medium. I suggest that the reason why clay is coagulated more readily in an alkaline medium only when the concentration of the alkali is above a certain value is that at these higher concentrations some of the clay is broken down into silicates (Oakley, *loc. cit.*) and thus behaves in flocculation like silica.

The Effect of Alkalis on the Flocculation of Silica.—Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 461) noticed that silicic acid is coagulated by sodium and calcium hydroxides at concentrations of 0·1 and 0·002, respectively, but not at all by the chlorides at a concentration of 0·07. These results have been confirmed for a silica suspension. The silica used in these experiments was purified by repeated treatments with hot concentrated hydrochloric acid, washed by decantation, and dialysed to a high specific resistance. It was then reduced to a finely divided state by repeated grinding in a wet condition in an agate mortar and sedimentation. In this way, a 1% suspension was obtained which remained in suspension for 2 hours. The following table gives the minimum concentration of

sodium required to cause coagulation of a 0·1% suspension in 1 hour, various mixtures of sodium chloride and sodium hydroxide being used. The experiments were made in test-tubes, the volume being 10 c.c., and 1 c.c. of the 1% suspension being added last.

The flocculation of silica by sodium chloride and hydroxide mixtures.

NaCl : NaOH.	Conc. NaOH, ×100.	Conc. Na, ×100.	p_H.	NaCl : NaOH.	Conc. NaOH, ×100.	Conc. Na, ×100.	p_H.
0 : 1	9·0	9	12·21	300 : 1	0·14	42	9·21
10 : 1	1·2	12	11·13	500 : 1	0·11	55	8·73
25 : 1	0·56	14	10·53	1000 : 1	0·07	70	8·20
50 : 1	0·40	20	10·06	2000 : 1	0·045	90	7·27
100 : 1	0·26	26	9·77	1 : 0	0·00	100	No flocc.
200 : 1	0·18	37	9·54				

Some of these results are plotted in Figs. 2 and 3. Above a p_H of 10, the points for silica lie close to the curve for kaolin, but with a decrease in the p_H the flocculating concentration for silica continues to increase rapidly, whereas for kaolin and clay it shows a sudden decrease.

The Flocculation of Silica by Alumina.—It was thought that this difference in the flocculating concentrations for clay and silica might be connected with the presence of combined alumina in the former substance, and it was accordingly decided to precipitate small quantities of alumina on silica and to find out how this product behaved towards coagulation by mixtures of sodium chloride and hydroxide.

In the following experiments the effect of sodium hydroxide on the coagulation of silica by aluminium chloride was studied. The order of adding the reagents has an effect. In these experiments the 1% silica suspension was always added to the aluminium chloride solution, and the sodium hydroxide was added last. The final concentration of silica was 0·1%. The following scheme summarises the results. The sign of the charge of the resultant suspension was determined by cataphoresis in a U-tube.

Flocculation of a 0·1% silica suspension by aluminium chloride and sodium hydroxide.

$AlCl_3$ (mol. per litre).	NaOH (mol. per litre).	Sign of charge.	Whether flocculated or not.	p_H.
<0·0001	0	—	Deflocculated	
0·0001	0	Neutral	Flocculated slowly	2·4
>0·0001	0	+	Deflocculated	
0·0001	<0·0002	Neutral	Flocculated slowly	
0·0001	0·0002	Neutral	Flocculated	5·3
0·0001	>0·0002	—	Deflocculated	
0·001	<0·003	+	Deflocculated	
0·001	0·003	Neutral	Flocculated	8·5
0·001	>0·004	—	Deflocculated	

Small quantities of aluminium chloride flocculate silica, but larger quantities give a stable electropositive suspension. The addition of sodium hydroxide in quantities approximately equivalent to the aluminium chloride rapidly flocculates the silica, but the p_H at which this most rapid flocculation takes place depends on the concentration of aluminium chloride. The further addition of sodium hydroxide results in the formation of a stable electronegative suspension. I think these results are most simply accounted for by supposing the particles of the electropositive suspensions to be coated with aluminium hydroxide, which therefore imparts the properties of a suspension of this substance to the silica. Thus, like aluminium hydroxide, it is electropositive and is easily flocculated by the addition of sodium hydroxide. With the further addition of caustic soda, a surface layer of sodium aluminosilicate is formed, which, like clay, is electronegative owing to surface ionisation into sodium ions and insoluble aluminosilicate ions. This substance should therefore behave like clay with regard to flocculation by mixtures of sodium chloride and hydroxide.

The Preparation and Flocculation of "Aluminated" Silica.—A stock of silica coagulated with aluminium hydroxide was prepared by adding to a 1% suspension of silica, water, aluminium chloride, and then sodium hydroxide in amounts to make the final concentrations 0·5% of silica, 0·001*M*-aluminium chloride and 0·0023*N*-sodium hydroxide. To obtain coagulation, it was necessary to determine these concentrations with some care by making initial trials on small quantities. The suspension was centrifuged, the supernatant liquid decanted, and water added to the residue to make the suspension 1%. This was stable when diluted to 0·1%. The settled material was about four times as bulky as silica. A series of flocculation experiments using mixtures of sodium chloride and hydroxide was then made on 0·1% suspensions in test-tubes as with silica: the results are plotted as triangles in Figs. 2 and 3. An exactly similar series of observations was made on a pure suspension of kaolin: these results are shown as crosses in the figures. The curves for the two substances have closely similar characteristics, although the maximum in both cases is less pronounced than for clay.

Both "aluminated" silica and kaolin showed successive flocculation, deflocculation, and flocculation on the addition of increasing quantities of alkaline sodium chloride, provided the ratio of chloride to hydroxide was not less than 250 : 1. Silica, however, does not show this phenomenon. The following scheme compares the behaviour of the three substances towards flocculation by a 300 : 1 mixture of sodium chloride and hydroxide. The negative sign

indicates no flocculation and the positive sign flocculation after 1 hour. It should be mentioned that these results were obtained on a suspension of "aluminated" silica only 2 or 3 days old; a few experiments on a preparation which had been standing several months showed a change in the concentrations required for flocculation.

Conc. of $Na^{\cdot}$ ion, $\times 10^3$.	Silica.	"Aluminated" silica.	Kaolin (10118).
3	−	−	−
5	−	−	+
7	−	+	+
10	−	+	+
15	−	+	+
20	−	+	−
30	−	+	−
40	−	−	−
50	−	−	−
70	−	+	−
100	−	+	−
150	−	+	−
180	−	+	+
450	+	+	+

Comparison of the Flocculating Powers of Sodium Hydroxide, Carbonate and Bicarbonate.—As might be anticipated from the curves in Fig. 3, sodium hydroxide flocculates at a lower concentration than the carbonate, which in turn flocculates at a lower concentration than the bicarbonate, since this is the order of decreasing alkalinity of the three compounds. This is illustrated in the following table:

Concentration of alkali required to flocculate in 1 hour.

Clay.	NaOH.	Na_2CO_3.	$NaHCO_3$.
Gezira (10195)	0·05	0·30	0·35
Mongalla (18107) (red)	0·21	0·32	0·32
Kaolin (10118)	0·09	0·40	0·42
Silica	0·09	0·42	0·95
"Aluminated" silica	0·09	0·25	0·60

In the present paper, I have purposely omitted any discussion of the mechanism of flocculation, owing to the absence of any really satisfactory theory of the phenomenon for colloids in general, but I think that the maxima and minima in the curves of Fig. 1 can be regarded as the outcome of two opposing factors in the stability of clay. The first factor, which tends to stabilise the suspension, is the formation of a sodium compound with the clay; the extent to which this takes place will depend upon the reaction of the medium and the concentration of sodium ions, and reaches a limit between p_H 9 and 10 (Oakley, *loc. cit.*). The second factor, which tends to flocculate the suspension, is the concentration of electrolyte in solution. With increasing concentrations of slightly alkaline

sodium chloride, the clay is first flocculated at a low concentration because it remains essentially an "acid clay" and contains no sodium to stabilise it. With higher concentrations, sodium is absorbed in increasing quantities until the sodium–clay complex is sufficiently lyophilic to withstand quite high concentrations of sodium chloride, but the concentration at which this second deflocculation takes place will depend on the alkalinity of the mixture used, being lower the greater the concentration of alkali until, with strongly alkaline mixtures, sodium–clay compounds are formed from the start and no minimum occurs in the flocculation curve. The deflocculated sodium clay is finally flocculated by increasing concentration of electrolyte.

With regard to the mechanism of flocculation, the theory of mutual electrical repulsion between the particles is very inadequate, as McBain has pointed out (*Colloid Symposium Monograph*, 1926, **4**, 13). I think the views put forward by Duclaux (*J. Chim. phys.*, 1909, 405) on the importance of osmotic forces in colloidal solutions and suspensions offer the most hopeful starting point in the development of an adequate theory of their stability.

Summary.

1. Certain mixtures of sodium, potassium, lithium, or calcium chloride with the respective hydroxide, when added in increasing amounts to a purified clay suspension, at first flocculate, then fail to flocculate, and finally flocculate the clay again. The phenomenon is shown by kaolin and also by silica coagulated by a small quantity of alumina, but not by pure silica, and it fails only when the suspensions are alkaline. The flocculating powers are in the increasing order: lithium, sodium, potassium, calcium, the last being about 10 times as powerful as sodium.

2. There is a pronounced maximum between a p_H of 9 and 10 in the concentration of sodium or calcium chloride required to flocculate clay or kaolin. The "aluminated" silica is remarkably similar to kaolin in respect of the influence of alkalis on the concentration of sodium chloride required for flocculation, and both these substances have similar characteristics to clay with regard to flocculation.

3. Silica is flocculated by sodium or calcium chloride only when the medium is alkaline. The minimal concentration required for flocculation rises rapidly as the alkalinity diminishes.

4. Silica is flocculated by 0·0001*M*-aluminium chloride; greater concentrations give a stable electropositive suspension. The subsequent addition of small quantities of sodium hydroxide at first flocculates the suspension and then gives a stable electronegative suspension.

5. Clay is more readily flocculated by calcium hydroxide than by calcium chloride at equivalent concentrations provided the concentration exceeds 0·003*N*. Below this concentration calcium chloride is the better flocculant.

I wish to express my appreciation of the helpful interest of Dr. A. F. Joseph in this work.

WELLCOME TROPICAL RESEARCH LABORATORIES,
KHARTOUM. [*Received, June 29th*, 1927.]

CCCCVI.—*The Interaction of Bromine with Acetic Anhydride. Part III. Arrest of the Reaction. A Comparison with the Bromination of Acetone.*

By HERBERT BEN WATSON.

THE powerful negative catalytic effect of quinoline and the less marked influence of certain other basic substances on the bromination of acetic anhydride have been referred to in Part II (this vol., p. 2458). The author finds that the reaction of bromine with acetone can be arrested in a similar manner. When bromine is added to acetone in carbon tetrachloride at 25°, no measurable reaction occurs for a short time; the disappearance of bromine then becomes perceptible, and almost immediately attains great speed, owing to the very powerful catalytic effect (Meyer, *Annalen*, 1911, **380**, 238) of hydrogen bromide upon enolisation in non-ionising solvents. Addition of a trace of quinoline arrests the reaction during a long period, and it seems simplest to suggest that the arrest is due to removal of hydrogen bromide as the hydrobromide (or hydrobromide perbromide, Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124; Trowbridge, *J. Amer. Chem. Soc.*, 1899, **21**, 66) of the base. The well-known inhibition, by certain nitrogen-containing compounds, of gaseous photochemical reactions has been interpreted in terms of the energetics of the system (Chapman and MacMahon, J., 1909, **95**, 1718; 1910, **97**, 847) and of surface phenomena (Norrish, J., 1925, **127**, 2319), but the view here put forward of the influence of quinoline on a reaction which takes place in the liquid phase and in the dark appears to account for the observed facts.

A similar interpretation may be applied to the case of acetic anhydride, and is rendered the more probable by the fact that quinoline is without effect in presence of 1·6 equivalents of sulphuric acid. The reaction of the base with the halogen acid produced in the bromination of the enolised anhydride will prevent the formation of any appreciable quantity of acetyl bromide (or any acetyl bromide

formed may be converted into an additive compound with quinoline; Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 1408); the main series of reactions, involving the bromination of the acid bromide, is thus eliminated until sufficient hydrogen bromide has been formed (in the slow change through the enolised anhydride) to react with the whole of the base. Moreover, removal by the quinoline of the greater part of the hydrogen bromide normally present in the equilibrium $(CH_3{\cdot}CO)_2O + HBr \rightleftharpoons CH_3{\cdot}CO_2H + CH_3{\cdot}COBr$ (Part II, p. 2459) renders the enolisation of the anhydride so slow as to be imperceptible; the values of k' given in Part II refer to the rate of enolisation in presence of this hydrogen bromide. The prolonged period of inertness is thus explained. The shorter duration of this period in presence of pyridine, *iso*quinoline, triethylamine, or dimethylaniline may be attributed to a larger amount of hydrogen bromide present in equilibrium with the base and its hydrobromide, $B,HBr \rightleftharpoons B + HBr$. The relatively feeble effect of aliphatic primary and secondary amines is to be expected, since they can be acetylated by the anhydride, as is also the complete inactivity (and even slight accelerating influence) of aniline and monomethylaniline, which are not only acetylated, but also substituted in the benzene nucleus, hydrogen bromide being evolved.

The effect of acetyl nitrate (Part II) also may be ascribed to the removal of hydrogen bromide (and perhaps of acetyl bromide), with consequent elimination of the main series of reactions and the rendering of the enolisation of the anhydride imperceptibly slow. That the removal is here due to oxidation is indicated by a considerable liberation of bromine when acetyl bromide is added to acetic anhydride containing nitric acid. Addition of 4 mols. of acetyl bromide per mol. of nitric acid completely annuls the effect of the latter, while on further addition of the acid bromide the disappearance of bromine is accelerated in the normal manner. Acetyl nitrate also retards the bromination of acetone, but does not arrest the reaction completely, as quinoline does. Nitric acid, on the other hand, shortens the time needed for the reaction to become perceptible (compare Lapworth, J., 1904, **85**, 31).

The arrests referred to in Part II may be attributed, in general, therefore, to the removal of hydrogen bromide (and perhaps sometimes of acetyl bromide) as a consequence of either the basic or the oxidising quality of the inhibitor.

EXPERIMENTAL.

Bromination of Acetone in Carbon Tetrachloride.—The carbon tetrachloride was shaken with aqueous sodium hydroxide and then with water, dried, and fractionated. Acetone, purified by the

sodium iodide method, was dried over calcium chloride and fractionated. The quinoline was dried over solid potassium hydroxide and fractionated, and the nitric acid was distilled from sulphuric acid and freed from nitrous acid by passage of carbon dioxide. The velocity determinations were carried out by withdrawal at intervals of 2 c.c. of the reaction mixture, addition to aqueous potassium iodide, and titration of the iodine. In Table I, titres are expressed as c.c. of $N/50$-thiosulphate.

TABLE I.

Acetone = 0·218M.		Acetone = 0·109M.		Acetone = 0·218M.	
Time (mins.).	Titre.	Time (mins.).	Titre.	HNO_3 = 0·025M.	
0	14·48	0	13·98	Ac_2O = 0·030M.	
9	14·48	10	13·92	Time (hrs.).	Titre.
10	14·42	12	13·88	0	12·48
10·5	14·32	13	13·85	1	12·32
11	13·98	14	13·60	7·5	11·62
11·5	0	15	0	22·5	10·05
				31	9·32
Acetone = 0·218M.		Acetone = 0·218M.		46	8·05
HNO_3 = 0·025M.		Quinoline = 0·003M.		70	5·95
Time (mins.).	Titre.	Time (hrs.).	Titre.	119	3·75
0	12·48	0	12·58	166	1·62
5	12·48	164	12·55		
7	0	222	12·45		
		232	0		

Bromination of Acetic Anhydride.—Purification of materials and experimental procedure were as described in Part II. Titres in Table II are expressed as c.c. of $N/10$-thiosulphate. Reactions I(d) and II(b) are identical with the reaction of bromine with pure acetic anhydride.

TABLE II.

I. Effect of quinoline and sulphuric acid in conjunction; quinoline = 0·0064M.

	Ratio, $\frac{1}{2}H_2SO_4/C_9H_7N$.	Initial titre.	Fall in titre after (mins.) 10.	20.	30.	40.	50.	60.
(a)	1·01	10·35	0	0	0	0	0	0
(b)	1·27	10·15	0	0	0·02	0·60	1·55	3·00
(c)	1·48	9·95	0·05	0·60	1·88	3·30	4·60	5·85
(d)	1·62	10·22	0·20	1·58	2·92	4·38	5·75	7·08
(e)	1·82	10·52	0·82	2·20	3·82	5·45	6·75	8·10

II. Effect of nitric acid and acetyl bromide in conjunction; HNO_3 = 0·0032M.

	Ratio, AcBr/HNO_3.	Initial titre.	Fall in titre after (mins.) 15.	30.	45.	60.	75.	90.
(a)	2·0	10·75	0	0	0	0	0	0
(b)	4·3	10·70	0·72	2·55	4·68	6·72	8·18	9·10
(c)	7·3	11·15	0·75	4·10	6·60	8·22	9·32	9·95
(d)	13·4	10·75	2·32	5·30	7·30	8·68	9·60	—

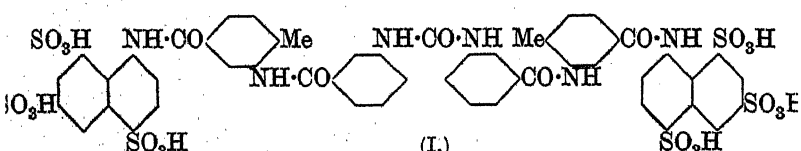
In conclusion, the author wishes to express his thanks to Professor K. J. P. Orton, F.R.S., for much helpful advice and criticism, to Dr. H. I. Hughes for carrying out some of the experiments, and to the Chemical Society for a grant towards the expenses of the research.

UNIVERSITY COLLEGE OF NORTH WALES,
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CCCCVII.—*Trypanocidal Action and Chemical Constitution. Part VII. s-Carbamides and Arylamides of Naphthylamine-di- and -tri-sulphonic Acids with Some Observations on the Mesomorphic State.*

By ISIDORE ELKANAH BALABAN and HAROLD KING.

THE discovery of the substance known as Bayer 205 marks an epoch both in the development of chemotherapy and in the treatment of trypanosomiasis. The chemical identity of this substance remained for long undivulged owing to war conditions, but the group of substances of which it is a member was plainly covered by a series of patents taken out by the firm of Bayer from 1914 onwards (D.R.-P. 278122, etc.). The structure was elucidated by Fourneau, Tréfouel, and Vallée (*Ann. Inst. Pasteur*, 1924, **38**, 81), who showed that Bayer 205 was in all probability the *s*-carbamide of *m'*-aminobenzoyl-*m*-aminotoluoyl-1-naphthylamine-4 : 6 : 8-trisulphonic acid (I).



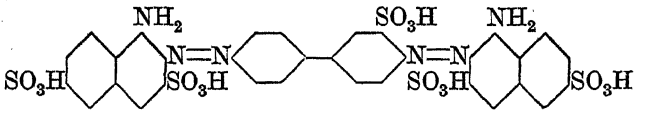
(I.)

It is natural that the discovery of an intensely trypanocidal agent like Bayer 205, colourless and containing no metallic group to which its toxic properties might be referred, should stimulate enquiry into the general principles governing its mode of action. On this point the patents are not informative, but Heymann (*Z. angew. Chem.*, 1924, **37**, 585) and Röhl (*Arch. Schiff. Trop. Hyg.*, 1926, **30**, *Beiheft* **1**, 103), both of the firm of Bayer and representing respectively the chemical and the pharmacological side, have contributed considerably to an insight into the general principles involved.

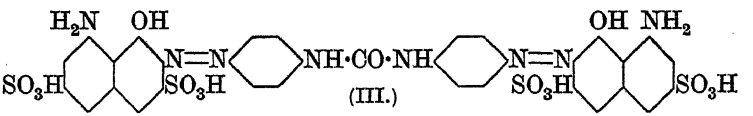
As early as 1904 Ehrlich and Shiga made the fundamental dis-

covery that Trypan-red (II), a member of the Congo-red series of cotton dyes, can cure an experimental infection of trypanosomiasis in mice.

(II.)



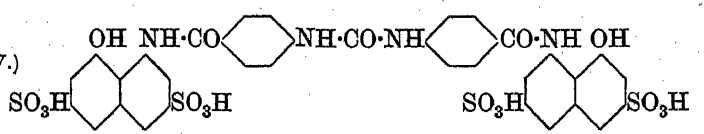
Following on this, Nicolle and Mesnil, in a classic paper (*Ann. Inst. Pasteur*, 1906, **20**, 417), examined a long range of cotton dyes all belonging to the Congo-red type and found the substance having the best curative action on infection with *Trypanosoma gambiense* in rats and monkeys to be the *s*-carbamide (III), a derivative of 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) called Afridol Violet.



(III.)

There are obvious disadvantages in dyes as therapeutic agents when applied to man or cattle, and if the therapeutic action of dyes is due to fixation by tissues it should be possible to prepare colourless substances of similar build and similar properties. The chemists of the firm of Bayer therefore chose as their starting point H-acid and prepared (IV), the colourless analogue of (III).

(IV.)



This substance delayed the death of mice suffering from trypanosomiasis by one day. Now from contemporaneous work on *dyes* it was known that substantive character to cotton was favoured by the presence of chains of aminobenzoyl groups and by the linking of these by carbonyl chloride. When, therefore, the aminobenzoyl groups in (IV) were duplicated in chain formation there was an increase of activity, but a falling off when they were triplicated. By chemical evolution from this striking discovery there resulted the gradual elaboration of the substance Bayer 205. It is quite clear from Heymann's account that the discovery of Bayer 205 arose from the recognition of the fact that it is possible to prepare colourless substances of substantive properties, which, being of similar molecular build to trypanocidally active dyes, also exhibit trypanocidal properties.

Röhl (*loc. cit.*), while also recognising the substantive properties

of these colourless substances, made the significant observation that these colourless complex carbamides form precipitates at very high dilutions with some of the simplest basic proteins, *e.g.*, clupeine, salmine, thymine, and sturine—constituents of the spermatozoa of fish. As a consequence, he supposes that the action of Bayer 205 on trypanosomes is due to a combination of the sulphonic acid groups with basic cell constituents of the parasites forming difficultly soluble salts.

Although the outline of a plausible picture of the principles underlying the action of Bayer 205 has been presented, no experimental evidence has been adduced in support of it. The work detailed in this communication was therefore undertaken in order to familiarise ourselves with this important field and to test the views which have been advanced.

For this purpose six readily accessible naphthylaminedisulphonic acids have been used as a starting point, *viz.*, Freund's acid (1-naphthylamine-3 : 6-disulphonic acid), amino-G-acid (2-naphthylamine-6 : 8-disulphonic acid), C-acid (2-naphthylamine-4 : 8-disulphonic acid), amino-J-acid (2-naphthylamine-5 : 7-disulphonic acid), H-acid (8-hydroxy-1-naphthylamine-3 : 6-disulphonic acid), and 2R-acid (8-hydroxy-2-naphthylamine-3 : 6-disulphonic acid).

These with the exception of H-acid have been converted into their *s*-carbamides, H-acid under the same conditions yielding the internal *ON*-carbonyl derivative, 1 : 8-ON-*carbonylaminonaphthol*-3 : 6-*disulphonic acid*. They have also been converted into their *m*-nitrobenzoyl derivatives and these in turn into the *m*-aminobenzoyl derivatives. The latter have been phosgenated to form the *s*-carbamides and have also been converted into the *m'*-nitrobenzoyl-*m*-aminobenzoyl derivatives. The latter have finally been reduced to the *m'*-aminobenzoyl-*m*-aminobenzoyl derivatives, which on phosgenation have given the *s*-carbamides. The general scheme of synthesis is shown below:

$$\begin{array}{rl} & NH_2R \longrightarrow RNH\cdot CO\cdot NHR \\ & NO_2\cdot Bz\cdot NHR \quad (\textit{First carbamide}) \\ \text{(1st)} & NH_2\cdot Bz\cdot NHR \longrightarrow RNH\cdot Bz\cdot NH\cdot CO\cdot NH\cdot Bz\cdot NHR \\ & NO_2\cdot Bz\cdot NH\cdot Bz\cdot NHR \quad (\textit{Second carbamide}) \\ \text{(2nd)} & NH_2\cdot Bz\cdot NHBz\cdot NHR \longrightarrow RNH\cdot BzNH\cdot BzNH\cdot CO\cdot NHBz\cdot NHBz\cdot NHR \\ & \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (\textit{Third carbamide}) \end{array}$$

$$(Bz = \cdot C_6H_4\cdot CO\cdot)$$

These have all been isolated in a state of purity free from sodium chloride and, excluding the nitro-compounds, have been tested for toxicity on normal mice and for trypanocidal action on mice infected experimentally with *T. equiperdum*. The maximum doses

tolerated by mice expressed in milligrams per gram of mouse are given in the following table :

	Aminobenzoyl derivatives.		Carbamides.		
	First.	Second.	First.	Second.	Third.
Freund's Acid	4·0	3·25	>2·0	1·5	0·4
Amino-G-Acid	1·5	1·0	1·75	**0·5**	**0·2**
C-Acid	3·0	1·0	2·0	**1·0**	**0·3**
Amino-J-Acid	3·0	0·75	1·75	**1·0**	0·3
H-Acid	2·25	1·0	3·0 *	**0·3**	**0·3**
2R-Acid	>2·5	0·7	2·0	0·1	0·2

* *ON*-Carbonyl derivative.

It will be observed that there is a very rough parallelism between the corresponding derivatives of different acids. The only compounds showing any trypanocidal action, and that of a low order as indicated below, are those carbamides the tolerated doses of which are expressed in heavy type. For these, the curative action is shown in the following table, each substance as a rule being tested on 4 or 5 infected mice, and r signifying the number of days before relapse occurred in the most favourable cases :

	Second carbamide.	Third carbamide.
Amino-G-Acid	0·3, $r = 4$	0·2, $r = 7$
C-Acid	0·5, $r = 5$	0·3, $r = 12$
Amino-J-Acid	0·5, $r = 1$	No action
H-Acid	0·2, $r = 5$	0·175, $r = 5$

The striking fact emerges from these results that trypanocidal activity only appears at the *s*-carbamide stage of combination of the aminobenzoyl and aminobenzoylaminobenzoyl derivatives and that there is no trace of activity in any of the aminobenzoyl compounds. All the derivatives, moreover, of Freund's acid and of 2R-acid examined were inactive. This is contrary to the claim made in D.R.-P. 288273, where the *s*-carbamide of *m'*-aminobenzoyl-*m*-aminobenzoyl-1-naphthylamine-3 : 6-disulphonic acid is said to cause the disappearance of trypanosomes from the blood of infected animals at high dilutions. This particular substance had not the slightest detectable action on the course of infection of *T. equiperdum* in mice, and trypanosomes exposed to 1% concentration of it for 24 hours *in vitro* were not rendered non-infective by it.

As the efficacy of the above-mentioned active carbamides was of a very low order, it was deemed of interest to investigate the corresponding series of compounds from the parent 1-naphthylamine-4 : 6 : 8-trisulphonic acid * contained in Bayer 205, particularly as Fourneau *et alii* (*loc. cit.*) have recorded a chemotherapeutic index, C/T, of 1/12 for the *s*-carbamide of *m'*-aminobenzoyl-

* For brevity of nomenclature, this acid is hereinafter referred to as B-Acid following Fourneau (*loc. cit.*).

m-aminobenzoyl-1-naphthylamine-4 : 6 : 8-trisulphonic acid, and Röhl (*loc. cit.*) states that the simple *s*-carbamide of B-acid is weakly active.

The following table gives the tolerated and the curative doses observed for the parallel series of derivatives of B-acid.

		Aminobenzoyl derivatives.		Carbamides.		
	Acid.	First.	Second.	First.	Second.	Third.
Dosis tolerata ...	3·0	2·0	1·5	>4·0	1·0	0·3
Dosis curativa ...	None	None	None	4·0, $r > 30$ 2·5, $r = 15$	None	0·15, $r > 30$

This table supports the main conclusion drawn from the previous tables that trypanocidal activity is only found in the *s*-carbamides and is absent from the parent acids and their aminobenzoylated derivatives.

Substantive Properties and Trypanocidal Action.

Although the recognition of the substantivity of colourless substances, *i.e.*, their affinity for natural fibres, was in the minds of the discoverers of Bayer 205 and led to its development, the question arises whether the therapeutic action of Bayer 205 or any of its analogues is due to this substantive property. Fortunately, this can, at least to some extent, be submitted to the test of experiment.

As the result of preliminary trials on the dyeing at 100° of pure wool, silk, and cotton by two members of the Congo-red series of dyes, namely, Trypan-red and Trypan-blue, with and without the use of "assistants," it was found that cotton was the most suitable fibre and sodium chloride the best "assistant." The same conditions could now be applied to the invisible dyeing of cotton by the colourless series of substances synthesised and tested for trypanocidal activity as related above. A limitation is, however, imposed in that it is only possible to "develop" the invisibly dyed cotton in those instances where there is a free naphthol group present. This limits the applicability of this mode of detection of the degree of substantivity of these colourless substances to the derivatives of H-acid and 2R-acid. Accordingly each substance (0·01 g.) mentioned in the table below was dissolved in water (10 c.c.), sodium chloride (0·5 g.) added, and a cotton skein (0·5 g.) immersed in the solution. The solution was heated at 100° for 1½ hours; the cotton was then removed and washed five times by decantation with water, 50 c.c. each time, and the colour was developed on the cotton by immersion in neutral diazotised *p*-nitroaniline at 12° as recommended for developing colour on cotton in

dyeing practice. After thorough washing, the skeins of cotton were dried, and the colour intensities compared by means of a Lovibond tintometer. The same conditions were used with derivatives of 2R-acid except that 2·5% sodium chloride was used, higher concentrations having a salting-out effect even at 100°. The following table gives the relative colour intensities of the dyed skeins of cotton expressed in terms of the content of naphthol, the assumption being made that the azo-compounds formed from a given acid and its derivatives are all analogously constituted and of equal tinctorial value per unit naphthol molecule. The free acids, their first carbamides, and their first nitrobenzoyl derivatives are omitted from the table, as they were under these conditions devoid of substantive property.

	Aminobenzoyl derivatives.		Nitrobenzoyl derivatives.	Carbamides.	
	First.	Second.	Second.	Second.	Third.
H-Acid	1	2	1	4	6
2R-Acid	4	5	2	9	12

The salient feature of this table is the pronounced maximum of substantivity to cotton at the *s*-carbamide stage of combination exhibited by these colourless substances, which are built up on the type or model of the Congo-red series of cotton dyes. Now it is precisely at the *s*-carbamide stage of combination that trypanocidal activity appears, so that there seems to be a parallelism between the substantive property of these carbamides to cotton and their trypanocidal activity. When the same conditions were applied to wool there was no selective substantivity exhibited.

In further support of this parallelism, it has been shown that the most active of all trypanocidal agents, Bayer 205, is also substantive to cotton. This cannot be demonstrated by development on the fibre, since Bayer 205 will not couple with diazotised amines, but it can be effected by making use of the observations of Röhl that these complex carbamides form precipitates with some of the simplest basic proteins at high dilutions. For this purpose, clupeine sulphate was chosen, as it is readily obtained from herrings' roe. The sensitiveness of the test for the detection of Bayer 205 by clupeine sulphate is not very great, but it may be increased by addition of 20% sodium chloride solution, as is shown in the following table :

Dilutions of Bayer 205	1 in 5,000	1 in 10,000	1 in 50,000	1 in 100,000
1 C.c.+2 drops 1% clupeine sulphate	Ppt.	Turbid	Clear	Clear
Bayer 205 + 20% NaCl	1 in 5,000	1 in 10,000	1 in 50,000	1 in 100,000
1 C.c. + 2 drops clupeine sulphate...	Ppt.	Ppt.	Turbid	Faint turbidity

Higher concentrations of sodium chloride have a salting-out effect on the clupeine sulphate.

The absorption of Bayer 205 by cotton was investigated by means of this reaction in the following way: Skeins of cotton (0·1 g.) were extracted in succession with pure ether, absolute alcohol, and several changes of boiling water and then dried. They were added to a solution of Bayer 205 (1·5 c.c.) containing sodium chloride (0·3 g.) and heated at 100° in stoppered tubes for an hour. When cool, 1 c.c. was removed and treated with 2 drops of 1% clupeine sulphate. The results of a series of experiments with controls are in the following table:

Tube.	Contents.	Reagent 2 drops clupeine sulphate.
1, 2	1·5 c.c. of 1 in 50,000 Bayer 205 + 0·3 g. NaCl + 0·1 g. cotton.	Solution clear.
3, 4	1·5 c.c. of 1 in 50,000 Bayer 205 + 0·3 g. NaCl.	Standard turbidity for this dilution.
5, 6	1·5 c.c. of water + 0·1 g. cotton + 0·3 g. NaCl.	Solution clear.

It therefore follows that Bayer 205 at a dilution of 1 in 50,000 is removed by cotton in the presence of sodium chloride, the concentration of Bayer 205 falling below 1 in 100,000. It would be of great interest to apply this method of detecting the substantive property to cotton of these colourless substances to the trypanocidally active series of B-acid described above. Unfortunately, it is extremely difficult, especially with limited supplies of material, to free them from sodium chloride, the uncontrolled presence of which would interfere seriously with the tests.

It was naturally of interest to determine whether the variation of the substantive property with structure was paralleled by the insolubility of the complexes formed between the protamines and the sulphonic acids. For this purpose, the *m*-aminobenzoyl and *m'*-aminobenzoyl-*m*-aminobenzoyl derivatives of H-acid and 2R-acid and the corresponding *s*-carbamides were compared in respect of their precipitability at high dilutions by clupeine sulphate. It was found that the *s*-carbamides did not form complexes of outstanding insolubility, but rather that they were very slightly more soluble than the complexes with the corresponding amines.

It may therefore be suggested on the basis of the limited number of examples examined by us that there appears to be a rough parallelism between the substantivity to cotton and trypanocidal action *in vivo*, in that salient peaks of substantivity occur at the *s*-carbamide stage of combination and trypanocidal action is only found in the *s*-carbamides. The interpretation of this is probably that substantivity to cotton is paralleled by the substantivity either

to the tissues of the mammalian host or to the trypanosomes or to both.

The Mesomorphic State of Derivatives of Naphthylaminedisulphonic Acids.

The recognition of the mesomorphic or liquid crystalline state of matter is largely due to the pioneering labours from 1877 onwards of O. Lehmann. The development of the subject has been mainly confined to pure crystalline substances which when melted showed anisotropy or which, when converted into the isotropic liquid state by heat, developed the anisotropic fluid phase on cooling. This field has been especially enriched by Vörlander's syntheses of numerous organic compounds showing this property. Within the last few years an extension of the subject has taken place in that it has been shown that anisotropic fluids may separate from aqueous media and the richest field in this respect is that of the soaps.

It is historically of interest that the first anisotropic fluid ever observed belonged to the latter class. Virchow in 1854 (*Arch. path. Anat. Physiol.*, 6, 562) showed that the material separating from a hot alcoholic extract of brain tissue or spinal cord in contact with water swelled up with production of the so-called "myelin-forms" and in 1858 Mettenheimer made the important observation that the "myelin-forms" were anisotropic. There is little doubt that it is the combined fatty acids present in the phosphatides (lecithin, cephalin, phrenosin, etc.) which are primarily responsible for this property. In 1866, Neubauer (*ibid.*, 36, 303) obtained "myelin-forms" by exposure of oleic acid to ammonia, but Lehmann first recognised the crystalline fluid phase of the oleic acid salts (*Ann. Physik*, 1895, 56, 771). During subsequent years there are occasional references to be found to the anisotropy of soap solutions or to the anisotropy of "myelin-forms" produced from soaps (Krafft, *Z. physiol. Chem.*, 1902, 35, 364, 376; Adami and Aschoff, *Proc. Roy. Soc.*, 1906, 78, *B*, 30; Friedel, *Ann. Physique*, 1922, 18, 273). In 1923, however, Maclennan (*J. Soc. Chem. Ind.*, 42, 393) revealed the rich field of anisotropic fluids from aqueous solutions covered by the soaps and following on this McBain and Langdon (J., 1925, 127, 852) and McBain and Elford (J., 1926, 421) have given a full account of the set of equilibria which govern such systems.

The compounds described in this paper are rich in examples of anisotropic fluids from aqueous media and provide a wonderful wealth of material for quantitative study. So far they have only been examined qualitatively, and incidentally to the main theme of this communication, but the qualitative observations lead one

to believe that the whole group of phenomena are subject to the limitations imposed by the phase rule. Structurally the compounds exhibiting this property are far removed from the fatty-acid type and are more akin to the isolated cases of mesomorphy of 10-bromo- and 10-chloro-phenanthrene-3(or 6)-sulphonic acid of Sandqvist (*Ber.*, 1915, **48**, 2054; *Kolloid Z.*, 1916, **19**, 113; *Arkiv Kemi*, 1916, **7**, No. 2).

Of the compounds described in this paper, the phenomenon of mesomorphy is restricted to those derived from disulphonic acids of the naphthylamines and has been observed in derivatives of each of the disulphonic acids mentioned on p. 3070, but is particularly pronounced in derivatives of C-acid, amino-J-acid, and amino-G-acid. Among these derivatives, it may occur as early as the first *m*-nitrobenzoyl derivative and be found in all the subsequent derivatives up to the *s*-carbamide of the *m'*-aminobenzoyl-*m*-aminobenzoyl derivative. As a rule it seems to be the least pronounced in the *s*-carbamides.

Derivatives of the naphthylaminedisulphonic acids show a general resemblance in behaviour. They are soluble in hot water and on being allowed to cool usually give, not crystals which are amenable to filtration, but, rather, highly hydrated products which vary greatly in consistency; they may be waxy solids, limpid fluids possessed of a sheen, clear gels or worm-like growths, and are in almost all cases strongly birefringent. The high degree of hydration seems essential for their production, for, if allowed to form from 50% or higher strengths of alcohol, they usually separate in the solid crystalline state, a totally distinct phase amenable to filtration and processes of washing. It is only in this manner in many cases that it is possible to obtain the products pure and free from inorganic salts. As a rule, the products are readily salted out from aqueous solutions by sodium chloride in a caseous form which lends itself to filtration. It has not been possible to decide whether this caseous phase is a new phase, in the same sense that the curds obtained in the soap-boiling process are a new phase giving an *X*-ray pattern, unobtainable from the anisotropic fluid phase of soaps, or is merely a stage in the dehydration of the anisotropic fluids. Such qualitative evidence as we possess suggests that under the dehydrating action of sodium chloride or alcohol it is possible to pass gradually from a limpid anisotropic fluid in equilibrium with its saturated isotropic solution to the caseous form in equilibrium with a concentrated solution of sodium chloride or alcohol. The intermediate anisotropic fluid appears to possess a certain degree of rigidity, but always flows under pressure of a cover-slip. In many cases, the caseous form passes with lapse of

time into the crystalline solid phase, probably with some change in the degree of hydration. It follows from what has been said about the hydration of the anisotropic fluid phase that, if the pure solid crystalline form be redissolved in the minimum volume of boiling water, then, on cooling, the anisotropic fluid phase may separate and, owing to its high degree of hydration, may combine with the whole of the water present, giving a single anisotropic fluid phase. Such we believe we have observed in the case of the monosodium salt of *m*-aminobenzoyl-2-naphthylamine-5 : 7-disulphonic acid (see Experimental). In other cases, a biphasic fluid may result from equilibrium of the anisotropic fluid with its isotropic saturated aqueous solution. The stability of such solutions varies. The specific instance quoted above lends itself particularly to demonstration purposes, as the viscous anisotropic fluid may persist at room temperature for months and then pass into a sparingly soluble, microscopically fine crystalline solid in equilibrium with a limpid saturated solution. To the naked eye both conditions of the solution possess a sheen and are indistinguishable. In the case of the tetrasodium salt of the *s*-carbamide of *m'*-aminobenzoyl-*m*-aminobenzoyl-2-naphthylamine-6 : 8-disulphonic acid, it has been possible to observe, by means of the polarising microscope, the slow crystallisation of the solid phase at the expense of the surrounding anisotropic fluid. In other cases, the anisotropic fluid phase appears to be permanently stable, as samples have been kept for 2 years.

The converse phenomenon, formation of the anisotropic fluid phase at the expense of the crystalline solid phase, has been observed in the case of the disodium salt of *m'*-nitrobenzoyl-*m*-aminobenzoyl-2-naphthylamine-6 : 8 -disulphonic acid and in the case of the free acid, *m'*-nitrobenzoyl-*m*-aminobenzoyl-2-naphthylamine-4 : 8-disulphonic acid (see Experimental).

In appearance the anisotropic fluids, whether in presence of and in equilibrium with their saturated isotropic aqueous solutions or not, usually possess a sheen, and examined under the highest power of the microscope are never particulate. Under the polarising microscope they present alternations of dark and light patches and under pressure of a cover-slip show streaming of the light patches. The densities of the anisotropic fluid phase and the isotropic fluid phase in equilibrium are usually very close, as there is no evidence of settling, but on prolonged centrifuging a partial separation may be effected, the supernatant phase being clear and isotropic and the lower portion now exhibiting an orientation of the sheen in spiral form. The production of a sheen is by no means invariable, and cases are described in the experimental portion of clear anisotropic gels and of clear anisotropic viscous solutions.

The mimicry of crystalline form by liquid crystals has often been observed (Lehmann, Vörlander) and a good instance of such in aqueous media is presented by the sodium hydrogen salt of *m'*-aminobenzoyl-*m*-aminobenzoyl-2-naphthylamine-4 : 8-disulphonic acid.

The derivatives of 1-naphthylamine-4 : 6 : 8-trisulphonic acid, on the other hand, show none of these phenomena and as a rule are extremely soluble in water and salted out with difficulty. The following table shows the incidence of this property:

Salted out.	Not salted out.
RNH_2	$(RNH)_2CO$
NO_2·Bz·NHR	NH_2·Bz·NHR
NO_2·Bz·NH·Bz·NHR	$(RNH·Bz·NH)_2CO$
NH_2·Bz·NH·Bz·NHR (diNa salt)	NH_2·Bz·NH·Bz·NHR (triNa salt)
	$(RNH·Bz·NH·Bz·NH)_2CO$

It is of interest that the substance Bayer 205 (I), which only differs from the last member here tabulated by two methyl groups, is extremely soluble in water and is also not salted out. It occurs commercially as a white powder devoid of crystalline structure, but according to our own observations it may readily be crystallised by solution in a fraction of its weight of water, addition of several volumes of pure methyl alcohol, followed by gradual addition of acetone. It separates after some delay in clusters of needles.

It is a pleasure to recognise our indebtedness to the following: to Miss Durham and Miss Marchal of this Department for carrying out the many biological experiments; to Dr. A. Schedler of the Clayton Aniline Co. for gifts of pure wool, silk, and cotton; to Dr. J. T. Conroy of the United Alkali Co. for a free and liberal supply of carbonyl chloride, and to the Pharmazeutische Abteilung of the I.G. Farbenindustrie Aktiengesellschaft for a gift of 1-naphthylamine-4 : 6 : 8-trisulphonic acid.

Experimental.

m-Nitrobenzoyl-1-naphthylamine-3 : 6-disulphonic Acid.—1-Naphthylamine-3 : 6-disulphonic acid (Freund's acid, 12·1 g.) was dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) and 20 c.c. of water and treated with 14·85 g. (2 mols.) of *m*-nitrobenzoyl chloride, all at once, and the mixture was shaken for ½ hour with addition of a few drops of ether. Three successive portions (each 40 c.c.) of *N*-sodium hydroxide were then added at half-hourly intervals with subsequent shaking. The solution was made distinctly acid to Congo-paper, the *m*-nitrobenzoic acid removed by ether, the aqueous liquor neutralised to litmus and concentrated under reduced pressure at 50°, and two crops of the *disodium* salt collected (yield, 75%). This salt is readily soluble in water (1 in 26) and is precipitated in microscopic, triangular leaflets on addition of sodium chloride.

For analysis it was crystallised from 50% alcohol (Found: Loss at 140°, 16·3. $C_{17}H_{10}O_9N_2S_2Na_2,5\frac{1}{2}H_2O$ requires H_2O, 16·6%. Found in dried salt: Na, 9·1. $C_{17}H_{10}O_9N_2S_2Na_2$ requires Na, 9·3%). An aqueous solution of the salt is neutral to litmus and gives crystalline precipitates on addition of calcium, magnesium, and barium chlorides. The salt will also crystallise unchanged from solutions which are acid to Congo-paper.

m-*Aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—To a solution of 25 g. of the crude sodium salt (above described) in 195 c.c. of 2*N*-sodium hydroxide at 0°, ferrous chloride (70 g.; 7 mols.) in 100 c.c. of water was added slowly with stirring, followed by 195 c.c. of 2*N*-sodium hydroxide to make the solution definitely alkaline. After filtration the ferric hydroxide sludge was extracted twice with 250 c.c. of 0·2*N*-sodium hydroxide each time and the solution was neutralised and concentrated at 50°; the sparingly soluble azoxy-compound (1·7 g.) separated first, followed by the *disodium* salt (13·5 g.) of the required amino-acid. This crystallises from water, in which it is very readily soluble, in fine needles (Found: Loss at 160°, 16·6. $C_{17}H_{12}O_7N_2S_2Na_2,5H_2O$ requires H_2O, 16·2%. Found in anhydrous salt: Na, 9·5. $C_{17}H_{12}O_7N_2S_2Na_2$ requires Na, 9·9%). It gives a moderately easily soluble *diazo*-compound free from chloride but containing sodium, as a primrose-yellow precipitate of needles. This couples with glyoxaline derivatives in aqueous sodium carbonate, the solutions having a cherry-red colour. The disodium salt in concentrated solution gives a *calcium* salt, microscopic prisms, and a *barium* salt, sheaves of flat prisms, on addition of saturated calcium or barium chloride. The *silver* salt separates similarly as a microcrystalline powder.

The *sodium hydrogen* salt is much less soluble than the disodium salt and rapidly separated in flattened prisms when the latter (2·9 g.) in 5 c.c. of water was treated with 1 c.c. of concentrated hydrochloric acid (yield, 2·6 g.) (Found: Loss at 160°, 15·6. $C_{17}H_{13}O_7N_2S_2Na,4\frac{1}{2}H_2O$ requires H_2O, 15·4%. Found in anhydrous salt: Na, 5·1. $C_{17}H_{13}O_7N_2S_2Na$ requires Na, 5·2%).

The *azoxy-compound* is readily soluble in 8 parts of hot water and crystallises in yellow, silky, hair-like needles (Found: Loss at 95°, 18·5. $C_{34}H_{20}O_{15}N_4S_4Na_4,12H_2O$ requires H_2O, 18·6%. Found in anhydrous salt: Na, 9·2. $C_{34}H_{20}O_{15}N_4S_4Na_4$ requires Na, 9·7%).

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—The disodium salt of the preceding acid (10·7 g., 87% anhydrous salt) dissolved in 50 c.c. of water was nitrobenzoylated with two equivalents of acid chloride as described in the first stage of the synthesis. The final solution was made distinctly acid

Congo-paper and the gelatinous precipitate was collected and dissolved in water. The two solutions were then thoroughly extracted with ether, combined, neutralised, and concentrated at 50°, and the successive crops of gelatinous nitro-acid collected. These were dissolved in boiling water and treated with 10 volumes of alcohol and the solution was kept until the gelatinous nitro-compound which first separated had changed into a crystalline mass of soft, white needles (yield, 11 g.) (Found in product from 90% alcohol: Loss at 160°, 11·0. $C_{24}H_{15}O_{10}N_3S_2Na_2,4H_2O$ requires H_2O, 10·5%. Found in anhydrous salt: Na, 7·6. $C_{24}H_{15}O_{10}N_3S_2Na_2$ requires Na, 7·5%). This *nitro-amide* is readily soluble in water with a neutral reaction and couples only faintly with Pauly's reagent in sodium carbonate solution. It is fairly readily soluble in boiling methyl alcohol, but does not crystallise well from it.

m'-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—The preceding nitro-acid (10·2 g.) was reduced with ferrous chloride exactly as described at a previous stage. The alkaline filtrates and extracts of the ferric hydroxide were made neutral to Congo-paper; the thick, gelatinous precipitate which first separated soon became wholly crystalline (yield, 10·1 g.). The mother-liquors on concentration only deposited a further 0·25 g. This *amino-acid* is a *monosodium* salt and is soluble in 3 volumes of boiling water, separating as a thick felt of small, silky needles on cooling (Found: Loss at 160°, 24·0. $C_{24}H_{18}O_8N_3S_2Na,10H_2O$ requires H_2O, 24·2%. Found in anhydrous salt: Na, 3·9. $C_{24}H_{18}O_8N_3S_2Na$ requires Na, 4·1%). An aqueous solution of the salt colours Congo-paper faintly blue. The salt forms a sparingly soluble *diazo*-compound, crystallising in microscopic needles, which couples with alkaline β-naphthol with the usual red colour. The diazo-compound is free from chloridion but contains sodium.

s-*Carbamide of* 1-*Naphthylamine*-3 : 6-*disulphonic Acid*.—Freund's acid (5 g.) in 250 c.c. of water containing 35 g. (20 mols.) of anhydrous sodium carbonate was submitted to a slow stream of carbonyl chloride until the reaction was acid to Congo-paper. The main bulk of the carbamide had separated (5·1 g.). When dissolved in 33 c.c. of boiling water and neutralised to litmus paper, it separated on cooling in long, silky needles with a faint pink colour. It gave no reaction for amino-groups and was free from chloride (Found: Loss at 160°, 25·6. $C_{21}H_{12}O_{13}N_2S_4Na_4,14H_2O$ requires H_2O, 25·9%. Found in anhydrous salt: Na, 12·6. $C_{21}H_{12}O_{13}N_2S_4Na_4$ requires Na, 12·8%). This *carbamide* is soluble in cold water to the extent of 8%, but is very readily salted out by sodium chloride.

s-*Carbamide of* m-*Aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—Five g. of the *m*-aminobenzoyl amide were phosgenated as

described in the foregoing section. The solid which had separated was collected, dissolved in 50 c.c. of hot water, and inoculated with the needle form of the carbamide. The required carbamide then separated in balls of long, silky needles (yield, 3·75 g.). This *carbamide* separates from concentrated aqueous solutions in gelatinous, rounded masses which are optically anisotropic, showing black crosses under the polarising microscope. On keeping in more dilute solution, they become transformed into the needle form. It is also readily salted out in gelatinous, anisotropic masses (Found: Na, 7·2; loss at 160°, 21·7. $C_{35}H_{22}O_{15}N_4S_4Na_4,14\frac{1}{2}H_2O$ requires Na, 7·5; H_2O, 21·4%).

s-*Carbamide of* m'-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid.*—The phosgenation was carried out in the same way as the preceding. Complete separation of the partly precipitated carbamide was effected by addition of sodium chloride. The gelatinous solid from 6 g. of amino-compound was dissolved in 30 c.c. of hot water, neutralised, and treated with 7 volumes of alcohol. On keeping, the carbamide separated in finely divided and partly anisotropic particles free from chloride. The product was again crystallised and gave 3·6 g. of carbamide (Found: Loss at 160°, 17·0; Na, 6·2. $C_{49}H_{32}O_{17}N_6S_4Na_4,14H_2O$ requires H_2O, 17·4; Na, 6·3%). This *carbamide*, so prepared, is very soluble in water and separates from concentrated solutions in voluminous, anisotropic, waxy masses. It is precipitated by strong mineral acid as a fine, amorphous precipitate, but is only salted out with difficulty and yields a sparingly soluble, amorphous *barium* salt.

m-*Nitrobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid.*—Amino-J-acid (10·2 g. = 9·7 g. of anhydrous salt) in 100 c.c. of water was nitrobenzoylated as described above. After acidification, extraction with ether, and neutralisation the solution was concentrated at 50° and the successive crops were collected without washing, until sodium chloride began to separate. The crude solid was dissolved in 50 c.c. of hot water and treated with 50 c.c. of alcohol; it then gradually separated in clusters of small needles (yield, 15·2 g.) (Found: Loss at 160°, 16·9; Na, 7·4. $C_{17}H_{10}O_9N_2S_2Na_2,5\frac{1}{2}H_2O$ requires H_2O, 16·6; Na, 7·7%). This *nitro-amide* is extremely readily soluble in water, and very concentrated aqueous syrupy solutions deposit fibre- or worm-like anisotropic growths, at first, but on keeping, fine needles.

m-*Aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid.*—The nitro-amide was reduced at room temperature with ferrous chloride and alkali as described above. The combined alkaline filtrates and extracts of the ferric hydroxide on neutralisation to Congo-paper gave a copious, white, microcrystalline precipitate of the amino-

compound. The yield was practically quantitative. The solid was dissolved in the minimum volume of boiling water (about 30 volumes). When cold, the product consisted of an opaque, viscous, anisotropic fluid with elastic properties and possessed of a crystalline sheen. There was no separation into two phases on prolonged centrifuging. The liquid crystalline condition was unaltered by addition of dilute acids, but either alcohol or sodium chloride precipitated anisotropic gelatinous masses. On keeping for various periods, 5 days to 3 months, the viscous fluid passed spontaneously into a more stable condition with separation of microscopic needles in almost quantitative amount (Found: Loss at 160°, 14·4; Na, 4·6. $C_{17}H_{13}O_7N_2S_2Na,4H_2O$ requires H_2O, 14·0; Na, 4·4%). When diazotised in dilute acid solution, it yields a gelatinous *diazo-compound*. The *disodium* salt is extremely soluble in water, the solution soon becoming brown.

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid*.—The foregoing amino-compound (10·3 g.) in 170 c.c. of water was nitrobenzoylated as described for previous members. The final solution was neutral and contained the required nitro-amide in suspension as a finely-divided, crystalline solid. This was collected and the mother-liquors after removal of nitrobenzoic acid and concentration gave only a small quantity of nitro-amide. The combined solids crystallised from 150 c.c. of boiling water, with final addition of 150 c.c. of alcohol, in small, silky needles (yield, 14·0 g.) (Found: Loss at 160°, 21·1; Na, 5·6. $C_{24}H_{15}O_{10}N_3S_2Na_2,9H_2O$ requires H_2O, 20·9; Na, 5·9%). This *amide* is readily soluble in warm water and separates from the solution, on cooling, as a white, anisotropic, gelatinous mass. From very dilute solutions it separates in microscopic needles. Its aqueous solution is neutral to litmus, and sodium chloride produces an anisotropic, gelatinous precipitate.

m′-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5:7-*disulphonic Acid*.—The foregoing nitro-compound (7·7 g.) in 250 c.c. of water was reduced at 30—35° with ferrous chloride and alkali. The faintly alkaline mixture was stirred for 2 hours; all traces of the white, gelatinous ferrous salt had then disappeared. The filtrate and alkaline extracts of the ferric hydroxide on neutralisation to Congo-paper gave a gelatinous, anisotropic precipitate of the amino-compound. The mother-liquors gave a further small crop of 0·65 g. The product was crystallised from 125 c.c. of boiling water with addition of 125 c.c. of alcohol and gave 5·35 g. of soft balls of microscopic, silky needles of the *sodium hydrogen* salt (Found: Loss at 160°, 15·3; Na, 3·8. $C_{24}H_{18}O_8N_3S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 15·0; Na, 3·5%). This sodium salt is readily soluble in boiling water, and on cooling, the solution yields a white, turbid, anisotropic

fluid with a crystalline sheen. Clear aqueous solutions give gelatinous precipitates at high dilutions with 3*N*-hydrochloric acid. It diazotises and then couples in the usual way with β-naphthol. The *disodium* salt is readily soluble in cold water and crystallises in soft, woolly needles (Found: Loss at 160°, 17·1; Na, 6·3. $C_{24}H_{17}O_8N_3S_2Na_2,6\frac{1}{2}H_2O$ requires H_2O, 16·7; Na, 6·5%).

s-*Carbamide of* 2-*Naphthylamine*-5 : 7-*disulphonic Acid.*—When this naphthylamine was phosgenated in 50 volumes of water with sodium carbonate (20 mols.), there was no separation of solid, but on saturation with sodium chloride the carbamide was precipitated in short needles. It was collected and re-phosgenated under the same conditions and again precipitated. It was dissolved in hot water, neutralised, and crystallised by addition of 3 volumes of alcohol. It was recrystallised and gave 5·0 g. from 10·0 g. of the naphthylamine (Found: Loss at 160°, 14·4; Na, 11·0. $C_{21}H_{12}O_{13}N_2S_4Na_4,7H_2O$ requires H_2O, 14·9; Na, 10·9%). This *carbamide* retains chloride with persistency. It crystallises well in clusters of long needles and is very soluble in water.

s-*Carbamide of* m-*Aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid.*—The amino-compound (10 g.) was phosgenated twice as described in the preceding paragraph. The partial separation of leaflets was completed by saturation with sodium chloride. The product after neutralisation was twice crystallised from hot water by addition of 3 volumes of alcohol (yield, 9·9 g.) (Found: Loss at 160°, 22·1; Na, 7·3. $C_{35}H_{22}O_{15}N_4S_4Na_4,15H_2O$ requires H_2O, 22·0; Na, 7·5%). This *carbamide* is very soluble in water, crystallising therefrom in pointed leaflets, and is precipitated by sodium chloride in microscopic rods or narrow leaflets. Addition of concentrated hydrochloric acid to a warm solution precipitates leaflets, possibly of a free sulphonic acid. The *barium* salt is sparingly soluble and crystallises in leaflets.

s-*Carbamide of* m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid.*—Five g. of the amino-compound in 500 c.c. of water were phosgenated in the usual way. The resultant acid product consisted of an opalescent jelly similar to raw white of egg. It was optically anisotropic and devoid of visible particles. When neutralised, it became definitely biphasic to the eye with separation of the sodium salt. Separation was completed by addition of sodium chloride. The product was collected, dissolved in 120 c.c. of boiling water, and treated with 120 c.c. of alcohol. If the alcohol be omitted, the solution sets to a clear anisotropic gel. The product from 50% alcohol was amorphous (yield 3·6 g.) (Found: Loss at 160°, 10·3; Na, 6·5. $C_{49}H_{32}O_{17}N_6S_4Na_4,8H_2O$ requires H_2O, 10·7; Na, 6·9%). This *carbamide* is readily precipit-

ated, possibly as the free sulphonic acid, by concentrated hydrochloric acid as a crystalline liquid, but from more dilute solutions, at first as a clear anisotropic gel but later in discrete crystalline growths. If the solution be heated and allowed to cool, it deposits circular tufts of leaflets. The *calcium* and *barium* salts are both sparingly soluble.

m-*Nitrobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—C-Acid (12·0 g = 9·7 g. of anhydrous monosodium salt) in 210 c.c. of water was nitrobenzoylated in the usual way. The solid which had separated was collected, dissolved in the minimum volume of water (900 c.c.), acidified, and extracted with ether. On neutralisation to litmus, the nitro-amide (12·8 g.) separated in a crystalline condition. The mother-liquors and the original mother-liquors of the benzoylation gave a further 2·5 g. on concentration. The solid crystallised from 9 volumes of boiling water in clusters of soft, pale yellow needles (Found: Loss at 160°, 15·2; Na, 7·6. $C_{17}H_{10}O_9N_2S_2Na_2,5H_2O$ requires H_2O, 15·4; Na, 7·8%). The most striking property of the salt is the ease with which it is salted out from aqueous solutions. Such solutions are neutral to litmus and give no precipitate with hydrochloric acid.

m-*Aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—The preceding nitro-amide (equivalent to 9·9 g. of anhydrous salt) was dissolved in 275 c.c. of water and reduced with ferrous chloride and alkali at room temperature. The alkaline extracts of the ferric hydroxide on neutralisation to Congo-paper deposited the main bulk of the required amino-acid, and the mother-liquors on concentration gave a further small quantity (yield, practically quantitative). It crystallised from the minimum volume of boiling water as a voluminous mass of soft, silky needles (Found: Loss at 160°, 18·6; Na, 4·3. $C_{17}H_{13}O_7N_2S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 18·2; Na, 4·2%). This *sodium hydrogen* salt is sparingly soluble in cold water, yielding a solution neutral to litmus. In dilute hydrochloric acid, it gives a sparingly soluble *diazosulphonate*, which separates in anisotropic, filamentous growths. The *disodium* salt was obtained by dissolving the hydrogen salt in a little water with the aid of sufficient sodium hydrogen carbonate to make the reaction faintly alkaline to litmus. It crystallised in fine needles, but it also occurs in plates. It is soluble in 10 volumes of water at room temperature (Found: Loss at 160°, 22·8. $C_{17}H_{12}O_7N_2S_2Na_2,7\frac{1}{2}H_2O$ requires H_2O, 22·5%. Found in anhydrous salt: Na, 9·7. $C_{17}H_{12}O_7N_2S_2Na_2$ requires Na, 9·9%).

m'-*Nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—The foregoing acid (10·2 g.) in 320 c.c. of water was nitrobenzoylated in the usual way. The final solution was clear, very viscous, and anisotropic. It was diluted with 400 c.c. of water,

acidified to Congo-paper, and extracted with ether. It was then neutralised to litmus, which restored the anisotropic gel condition. If the solution was more dilute, a gel was not formed, but anisotropic worm- or thread-like growths separated in quantity. These showed the phenomenon of black crosses under the polarising microscope, especially at the ends of growth. In either case, the solution was heated in the boiling water-bath and saturated with sodium chloride with stirring. When cold, the precipitated gelatinous solid was collected in quantitative yield, without washing. 5 G. of the air-dried material were dissolved in 75 c.c. of hot water and treated with 20 c.c. of concentrated hydrochloric acid. The solution rapidly deposited a thick felt of needles. These were filtered off, dissolved in 25 c.c. of hot water, and heated with 10 c.c. of concentrated hydrochloric acid. Fine, long needles rapidly separated, which were filtered off as dry as possible, rubbed on porous plate, and dried in a vacuum over sulphuric acid and sodium hydroxide. In this way, 2·35 g. of almost pure, anhydrous *disulphonic acid* were obtained free from chloride (Found: Na, 0·4%. 0·249 G. was equivalent to 8·2 c.c. of *N*/10-sodium hydroxide, agreeing with the value required for a mixture of 95% of disulphonic acid and 5% of disodium salt). A repetition of the procedure would probably remove the last traces of sodium. The disulphonic acid, treated with a little water, swells up, forming a clear, viscous, anisotropic fluid in equilibrium with the surrounding aqueous solution. More dilute solutions are clear and set to an anisotropic gel on addition of silver nitrate. If the crude crystalline disulphonic acid obtained after one treatment of the crude disodium salt with hydrochloric acid be dissolved in a small volume of hot water and treated with an equal volume of alcohol, the neutral *disodium* salt separates in soft balls of extremely minute needles (Found: Loss at 160°, 12·7. $C_{24}H_{15}O_{10}N_3S_2Na_2,5H_2O$ requires H_2O, 12·8%. Found in anhydrous salt: Na, 7·4. $C_{24}H_{15}O_{10}N_3S_2Na_2$ requires Na, 7·5%). The mother-liquors, however, are strongly acid to Congo-paper. This salt may be obtained directly from the original crude disodium salt by dissolving it in hot water and adding alcohol, but the process through the disulphonic acid is preferable. The disodium salt is moderately easily soluble in cold water and on addition of a little sodium chloride the solution sets to a clear anisotropic gel, a state also obtained by dissolving the disodium salt in warm water and allowing the solution to cool. This gel remains unchanged in a sealed vessel for many months. The *barium* and *calcium* salts are very sparingly soluble, the former crystallising in hairs. The *magnesium* salt crystallises in clusters of needles moderately easily soluble in water.

m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4:8-*disulphonic Acid*.—The foregoing disodium salt (7·6 g.) in 250 c.c. of water was reduced with ferrous chloride and alkali at 25°. The filtrate and alkaline extracts of the ferric hydroxide were made faintly acid to Congo-paper; the amino-compound then separated as a voluminous, anisotropic, gelatinous product which, on filtration, was left as a white, soapy solid. It was dissolved in 350 c.c. of boiling water and treated with an equal volume of alcohol; it then separated slowly in gelatinous, oat-shaped, anisotropic crystals (yield, 6·15 g.) (Found: Loss at 160°, 17·1; Na, 3·3. $C_{24}H_{18}O_8N_3S_2Na,6\frac{1}{2}H_2O$ requires H_2O, 17·2; Na, 3·4%). This *sodium hydrogen* salt is sparingly soluble in hot water, and a boiling saturated aqueous solution when allowed to cool gives two phases, a clear supernatant liquor and anisotropic aggregates simulating ill-formed, crystalline growths. On filtration on hardened paper under pressure, both phases passed through, yielding a macroscopically homogeneous filtrate with a crystalline sheen. Examined microscopically, it showed complete absence of particles, the whole fluid being anisotropic under polarised light. On prolonged centrifuging there is a separation of a clear aqueous upper layer and a more uniform orientation of the sheen in spiral form in the lower layer.

s-*Carbamide of* 2-*Naphthylamine*-4:8-*disulphonic Acid*.—This carbamide was prepared by a double phosgenation of the parent amine (5·0 g.), separation being completed by addition of sodium chloride. After neutralisation it was twice crystallised from water and separated in clusters of microscopic needles (yield, 3·5 g.) (Found: Loss at 160°, 11·3; Na, 11·1. $C_{21}H_{12}O_{13}N_2S_4Na_4,5H_2O$ requires H_2O, 11·1; Na, 11·3%). This *carbamide* is soluble in water at room temperature to the extent of 5%. It is not very readily salted out and is not precipitated by concentrated hydrochloric acid.

s-*Carbamide of* m-*Aminobenzoyl*-2-*naphthylamine*-4:8-*disulphonic Acid*.—For the preparation of this carbamide, 80 volumes of water were required and a double phosgenation was necessary. At the end of the phosgenation the crude carbamide separated in the liquid crystalline state, in the form of stringy, anisotropic masses. After saturation with sodium chloride, the product could be filtered off on hardened paper and after neutralisation with alkali it was dissolved in 9 volumes of hot water and treated with an equal volume of alcohol. The carbamide separated on keeping in clusters of small needles. The yield was 10·5 g. from 10·0 g. of initial material (Found: Loss at 160°, 18·4; Na, 7·5. $C_{35}H_{22}O_{15}N_4S_4Na_4,12H_2O$ requires H_2O, 18·4; Na, 7·8%). This *carbamide* is readily soluble in water, is fairly readily salted out, and is precipitated by excess

of concentrated hydrochloric acid in the liquid crystalline state; if, however, the solution be warmed and allowed to cool slowly, the carbamide separates in discrete crystalline growths. The *calcium* and *barium* salts are sparingly soluble, the latter notably so.

s-*Carbamide of* m'-*Aminobenzoyl*-m-*aminobenzŏyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—The parent amine (5 g.) was phosgenated in the usual way, and precipitation of the crude product completed by addition of sodium chloride. It was dissolved in 30 c.c. of boiling water, neutralised, and treated with 70 c.c. of alcohol. On keeping, the carbamide separated without definite recognisable structure, but the product was anisotropic (yield, 4·7 g.) (Found: Loss at 160°, 18·2; Na, 5·7, 6·1. $C_{49}H_{32}O_{17}N_6S_4Na_4,14\frac{1}{2}H_2O$ requires H_2O, 17·9; Na, 6·3%). This *carbamide* is soluble in water and crystallises from concentrated solutions in microscopic, circular, crystalline aggregates. It is readily precipitated, possibly as the free tetrasulphonic acid, by addition of concentrated hydrochloric acid in a similar crystalline form. The *magnesium*, *barium*, and *calcium* salts are sparingly soluble.

m-*Nitrobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—G-Acid (9·8 g. of anhydrous sodium hydrogen salt) in 120 c.c. of water was nitrobenzoylated in the usual way. The solution was diluted with 425 c.c. of water to dissolve the solid which had separated; it was then acidified and extracted with ether. After neutralisation the solution was concentrated at 50° and the successive crops of gelatinous solid were collected without washing. The combined crops were made up to 150 c.c. with boiling water, and 150 c.c. of alcohol added. On keeping, the nitro-amide separated in soft, woolly needles (yield, 14·55 g.) (Found: Loss at 160°, 19·9; Na, 7·7. $C_{17}H_{10}O_9N_2S_2Na_2,7H_2O$ requires H_2O, 20·3; Na, 7·4%). This *amide* is readily soluble in hot water and separates on cooling as an anisotropic, gelatinous phase, possibly a semi-rigid liquid crystalline phase, as it flowed when submitted to pressure under a coverslip. Addition of concentrated hydrochloric acid gave an anisotropic gelatinous precipitate, as also did the addition of sodium chloride, which even in small quantities has a salting-out effect.

m-*Aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The foregoing nitro-compound (12·4 g.) in 250 c.c. of water was reduced with ferrous chloride and alkali at 25°. On acidification, the filtrate and alkaline extracts of the ferric hydroxide gave a crystalline precipitate, and the mother-liquors on concentration a further small crop. These were dissolved in 50 c.c. of boiling water and treated with 20 c.c. of alcohol. The amide separated on cooling as a compact mass of needles (yield, 8·8 g.) (Found: Loss at 160°, 18·2. $C_{17}H_{13}O_7N_2S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 18·2%. Found in anhydrous

solid: Na, 5·1. $C_{17}H_{13}O_7N_2S_2Na$ requires Na, 5·2%). This *amide* is readily soluble in hot water. A hot concentrated solution, when cold, becomes transformed into a viscous liquid crystalline mass with a sheen. This remains unchanged when kept in a stoppered tube for months. The amide forms a sparingly soluble *diazo-compound*, crystallising in needles with a primrose-yellow colour.

m'-*Nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The preceding amino-compound (16·3 g.) in 370 c.c. of water was nitrobenzoylated in the usual way. The very viscous solution which resulted was acidified and mixed with an equal volume of alcohol. On keeping at 0°, the precipitate crystallised (yield, 19·5 g.). It separated from hot 65% alcohol in minute, soft needles (Found: Loss at 160°, 14·7. $C_{24}H_{15}O_{10}N_3S_2Na_2,6H_2O$ requires H_2O, 14·9%. Found in anhydrous solid: Na, 7·2. $C_{24}H_{15}O_{10}N_3S_2Na_2$ requires Na, 7·5%). This *amide* is soluble in 14 parts of boiling water and separates in anisotropic gelatinous globules. If the amide be left in contact with 18 volumes of water, the original white powder disappears and the whole of the fluid becomes a white elastic mass with a sheen. Under the polarising microscope it retained the anisotropic sheen and flowed under uneven pressure of the cover-slip. A hot solution treated with concentrated hydrochloric acid deposits a microcrystalline precipitate, possibly of the free disulphonic acid. The amide is very readily salted out and gives sparingly soluble precipitates with calcium, magnesium, and barium chlorides.

m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6:8-*disulphonic Acid*.—The preceding nitro-amide (17·4 g.) was dissolved in 600 c.c. of water at 30° and treated with 84 c.c. of 2*N*-sodium hydroxide. The solution set to a clear anisotropic gel, which gradually disintegrated on addition of 33·6 g. of ferrous chloride in 50 c.c. of water. Finally, a further 84 c.c. of 2*N*-sodium hydroxide were added, the final reaction being made faintly alkaline to litmus. After being stirred for 1 hour, the solution was warmed to 50° to ensure complete solution and reduction of the nitro-compound. The filtrate and alkaline extracts of the ferric hydroxide on acidification deposited the amino-compound in soft, matted, microscopic needles. Precipitation was completed by addition of sodium chloride. The collected solid was dissolved in the minimum volume (700 c.c.) of boiling water and treated with 350 c.c. of alcohol; on cooling, the amino-amide crystallised in clusters of soft, white needles (yield, 14·7 g.) (Found: Loss at 160°, 14·5; Na, 3·5. $C_{14}H_{18}O_8N_3S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 15·0; Na, 3·5%). This *amino*-compound is soluble in boiling water; the solution, on cooling, develops a white sheen, due to separation of the liquid crystalline phase. If a small amount of

sodium chloride be added to a clear dilute solution, this develops the liquid crystalline sheen, but only temporarily, the amide separating eventually in the solid crystalline condition. Hydrochloric acid also precipitates a liquid crystalline phase, and in very dilute hydrochloric acid a clear solution gives a liquid crystalline *diazosulphonate* on addition of sodium nitrite. The *disodium* salt is readily obtained as well-formed needles by dissolving the sodium hydrogen salt in warm sodium hydrogen carbonate solution and allowing it to cool. The *magnesium*, *calcium*, and *barium* salts are sparingly soluble in water.

s-*Carbamide of* 2-*Naphthylamine*-6 : 8-*disulphonic Acid*.—G-Acid (5 g.) was submitted to a thrice-repeated phosgenation under the usual conditions, sodium carbonate (20 mols.) being used each time. Separation of the solid was completed by addition of sodium chloride. After neutralisation it crystallised from boiling water, in which it was very soluble, in fine, colourless needles (Found : Loss at 160°, 19·9. $C_{21}H_{12}O_{13}N_2S_4Na_4,10H_2O$ requires H_2O, 20·0%. Found in the dried salt : Na, 12·6. $C_{21}H_{12}O_{13}N_2S_4Na_4$ requires Na, 12·8%). This *carbamide* has a sweet taste. It is readily soluble in water and is very readily salted out, in needles. It gives a sparingly soluble *barium* salt and with concentrated hydrochloric acid a precipitate of fine needles, probably the free tetrasulphonic acid.

s-*Carbamide of* m-*Aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The parent amino-compound (5 g.) was submitted to a treble phosgenation. Separation of the solid, which consisted of very fine, small needles, was completed by saturation with sodium chloride. The product was dissolved in 50 c.c. of hot water and neutralised. It separated in round, weakly anisotropic nodules, which coalesced on attempted washing. It was redissolved in 25 c.c. of water, and 25 c.c. of alcohol added ; it then slowly separated in clusters of needles (yield 3·5 g.) (Found in substance crystallised from water : Loss at 160°, 19·8. $C_{35}H_{22}O_{15}N_4S_4Na_4,13H_2O$ requires H_2O, 19·6%. Found in anhydrous salt : Na, 10·0. $C_{35}H_{22}O_{15}N_4S_4Na_4$ requires Na, 9·6%). This *carbamide* is very readily salted out. It gives sparingly soluble salts with magnesium, calcium, and barium chlorides. With concentrated hydrochloric acid it gives a precipitate of needles, probably the free tetrasulphonic acid.

s-*Carbamide of* m′-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The parent amino-compound (5 g.) was submitted to a double phosgenation. Separation of the carbamide was completed by addition of sodium chloride. It was then dissolved in 150 c.c. of boiling water with the aid of sufficient alkali to adjust the reaction to neutrality. To the hot solution 150 c.c.

of alcohol were added and on keeping the carbamide separated. It was again crystallised from 100 c.c. of water and 325 c.c. of alcohol (yield, 3·8 g.) (Found: Loss at 160°, 19·9. $C_{49}H_{32}O_{17}N_6S_4Na_4,16\frac{1}{2}H_2O$ requires H_2O, 19·9%. Found in anhydrous salt: Na, 7·6. $C_{49}H_{32}O_{17}N_6S_4Na_4$ requires Na, 7·7%). This *carbamide* separates from water–alcohol mixtures in weakly anisotropic, gelatinous particles. It is soluble in water; a hot concentrated solution on cooling deposits circular anisotropic clusters, but the surrounding aqueous medium also is anisotropic and flows under pressure of a cover-slip. Crystallisation of the solid phase proceeds at the expense of the liquid crystalline phase. Addition of dilute hydrochloric acid to a solution of the carbamide gives a clear anisotropic gel. The *magnesium*, *calcium*, and *barium* salts are sparingly soluble.

1-m-*Nitrobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—H-Acid (14·7 g.) was suspended in 70 c.c. of water with addition of 5·5 g. of hydrated sodium acetate (1 mol.) and nitrobenzoylated as described for earlier members. After acidification to Congo-paper, the heavy crop of crystals was collected, dried, and extracted with ether, leaving 18·2 g. of crude amide. The mother-liquors gave a further 2·6 g. on concentration. These combined crops were dissolved in boiling water and treated with a quarter of its volume of alcohol. On keeping, the pure amide separated in compact clusters of needles (Found: Loss at 120°, 19·3. $C_{17}H_{10}O_{10}N_2S_2Na_2,7H_2O$ requires H_2O, 19·7%. Found in anhydrous salt: Na, 8·9. $C_{17}H_{10}O_{10}N_2S_2Na_2$ requires Na, 9·0%). This *amide* is readily soluble in warm water and is not precipitated by concentrated hydrochloric acid. It is only salted out with difficulty and separates in a crystalline state. The *barium* salt, tufts of needles, is readily soluble in warm water but much less soluble in cold.

1-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The foregoing nitro-amide (12·8 g.) was reduced with ferrous chloride and alkali at 0° in the usual way. The filtrate and alkaline extracts of the ferric hydroxide on neutralisation gave a copious crystalline precipitate, which was collected, dissolved in 200 c.c. of boiling water, and treated with 100 c.c. of alcohol. After an interval, the pure amino-compound separated in delicate needles (yield, 9·3 g.) (Found: Loss at 160°, 17·4. $C_{17}H_{13}O_8N_2S_2Na,5H_2O$ requires H_2O, 16·4%. Found in dried salt: Na, 4·7. $C_{17}H_{13}O_8N_2S_2Na$ requires Na, 5·0%). This *sodium hydrogen* salt is not very soluble in warm water and it separates in anisotropic gelatinous particles. A dilute aqueous solution gives an immediate anisotropic precipitate on addition of dilute hydrochloric acid, probably of the disulphonic acid, which separates in microscopic leaflets if the solution be warmed

and allowed to cool. The *calcium*, *magnesium*, and *barium* salts are sparingly soluble, gelatinous precipitates. The *disodium* salt is very soluble in water and crystallises in needles.

1-m′-*Nitrobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The foregoing amino-compound (10·7 g.) was nitrobenzoylated as described at the previous stage. The resulting solution consisted of a viscous syrup containing anisotropic stringy or worm-like masses in suspension. It was diluted with 2000 c.c. of water, acidified, and extracted with ether. The solution was neutralised and then set to a clear anisotropic gel. It liquefied on rise of temperature and was concentrated at 50° to one-half its bulk and acidified with 200 c.c. of concentrated hydrochloric acid. This caused the precipitation of anisotropic liquid threads from which the mother-liquor could be decanted. When these were dissolved in hot water (140 c.c.) and treated with 280 c.c. of alcohol, the required salt separated in a filterable condition (yield, 11·8 g.) (Found: Loss at 160°, 17·4. $C_{24}H_{15}O_{11}N_3S_2Na_2,7\frac{1}{2}H_2O$ requires H_2O, 17·6%. Found in dried salt: Na, 7·3. $C_{24}H_{15}O_{11}N_3S_2Na_2$ requires Na, 7·3%). This *disodium* salt is soluble in boiling water and, on cooling, separates in anisotropic, worm-like growths. A dilute aqueous solution treated with a little sodium chloride sets to a clear anisotropic gel. Under the most favourable conditions for crystallisation—a little water and excess of alcohol—it separates in anisotropic, gelatinous aggregates devoid of recognisable structure.

1-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The preceding nitro-compound (9·0 g.) was reduced at 0° with ferrous chloride and alkali. The filtrate and alkaline extracts of the ferric hydroxide were neutralised to Congo-paper and on being kept for 24 hours deposited almost the whole of the amino-compound as an amorphous precipitate. This was dissolved in 100 c.c. of boiling water and treated with 50 c.c. of alcohol; it then separated slowly in the amorphous condition (Found: Loss at 160°, 16·9. $C_{24}H_{18}O_9N_3S_2Na,6\frac{1}{2}H_2O$ requires H_2O, 16·8%. Found in anhydrous salt: Na, 4·3. $C_{24}H_{18}O_9N_3S_2Na$ requires Na, 4·0%). This *sodium hydrogen* salt is not very soluble in boiling water. It separates on cooling in microscopic spicules or leaflets. Its dilute aqueous solution is precipitated by concentrated hydrochloric acid as a gelatinous, anisotropic product, which dissolves on warming and then crystallises in fine needles. It gives an orange colour on diazotisation.

ON-*Carbonyl*-1 : 8-*aminonaphthol*-3 : 6-*disulphonic Acid*.—H-Acid (5 g.) was dissolved in 100 c.c. of water containing 10 c.c. of 2*N*-sodium hydroxide and 20 g. of anhydrous sodium carbonate. The solution was phosgenated till acid to Congo-paper. The solid was

collected and crystallised from hot water (40 c.c.) (yield, 4 g.) (Found: Loss at 150°, 16·1. $C_{11}H_5O_8NS_2Na_2,4H_2O$ requires H_2O, 15·6%. Found in dried salt: Na, 11·8. $C_{11}H_5O_8NS_2Na_2$ requires Na, 11·8%). This *disodium* salt is soluble in 10 parts of cold water to a neutral solution. It crystallises in needles which darken on exposure to the air. It is readily salted out by sodium chloride and gives a very sparingly soluble *barium* salt. Unlike all the other derivatives of H-acid described in this paper, which give an intense magenta-red colour with Pauly's reagent in sodium carbonate solution, this salt gives no coloration.

s-*Carbamide of* 1-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid.*—Five g. of the aminobenzoylamide were submitted to a double phosgenation as described in previous instances. The precipitated solid was collected, dissolved in 15 c.c. of boiling water, neutralised, and treated with 7 c.c. of alcohol. The carbamide separated in clusters of gelatinous leaflets (yield, 3·0 g.) (Found: Loss at 160°, 19·8. $C_{35}H_{22}O_{17}N_4S_4Na_4,13\frac{1}{2}H_2O$ requires H_2O, 19·7%. Found in anhydrous salt: Na, 9·2. $C_{35}H_{22}O_{17}N_4S_4Na_4$ requires Na, 9·3%). This *carbamide* is soluble in boiling water and crystallises, on cooling, in the same way as from dilute alcohol. A solution in dilute nitric acid gives an orange-red solution on boiling. With magnesium, calcium, and barium chlorides it yields sparingly soluble, gelatinous precipitates.

s-*Carbamide of* 1-m'-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid.*—Five g. of the amino-compound were phosgenated in the usual way. The solution was saturated with sodium chloride, and the solid collected. It was dissolved in 260 c.c. of boiling water, neutralised, and treated with 200 c.c. of alcohol. The carbamide separated in gelatinous particles which were isotropic (yield, 3·3 g.) (Found: Loss at 160°, 20·6; Na, 6·0. $C_{49}H_{32}O_{19}N_6S_4Na_4,17\frac{1}{2}H_2O$ requires H_2O, 20·4; Na, 6·0%). This *carbamide* is not very soluble in water. It is readily salted out and gives sparingly soluble salts with magnesium, barium, and calcium chlorides.

2-m-*Nitrobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid.*—2R-Acid (24·2 g. of commercial disodium salt) was dissolved in 150 c.c. of water and nitrobenzoylated in the usual way. The highly coloured but clear solution was acidified to Congo-paper and on being kept for 12 hours at 0° gave 37 g. of crystalline solid, which, on ether extraction, gave 27·0 g. of amide. The original aqueous liquors after extraction with ether and concentration gave a further 4·2 g. of amide. The combined crops crystallised from 100 c.c. of water in small prisms (yield, 25·2 g.) (Found: Loss at 160°, 13·6. $C_{17}H_{10}O_{10}N_2S_2Na_2,4\frac{1}{2}H_2O$ requires H_2O, 13·7%. Found in anhydr-

ous salt: Na, 8·7. $C_{17}H_{10}O_{10}N_2S_2Na_2$ requires Na, 9·0%). This *disodium* salt is readily soluble in hot water but sparingly soluble in cold. It forms a *barium* salt, sparingly soluble in water, which crystallises in microscopic clusters of needles. This amide is readily salted out; it gives an eosin-like colour in sodium carbonate solution with Pauly's reagent. When boiled with dilute nitric acid it gives an orange-red solution.

2-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The above-described nitro-compound (20·8 g.) was reduced at 0° with ferrous chloride and alkali in the usual way. The filtrate and alkaline extracts of the ferric hydroxide on neutralisation to Congo-paper deposited 16·8 g. of small needles. The mother-liquor on concentration gave a further 2·1 g. The product was recrystallised from 10 volumes of boiling water (Found: Loss at 160°, 13·6. $C_{17}H_{13}O_8N_2S_2Na,4H_2O$ requires H_2O, 13·5%. Found in anhydrous salt: Na, 4·7. $C_{17}H_{13}O_8N_2S_2Na$ requires Na, 5·0%). This *amide* has a faint acid reaction to Congo-paper. It forms a *diazosulphonate*, fine needles, and it gives a sparingly soluble *barium* salt, granular crystals. It is very readily salted out.

2-m′-*Nitrobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The preceding amino-compound (10·6 g.) in 100 c.c. of water was nitrobenzoylated by the usual process. The final product was a clear anisotropic gel. Addition of a little concentrated hydrochloric acid gave a limpid fluid, but excess gave a clear anisotropic gel. This was stirred with sodium chloride; it then coagulated and could be filtered. It was dissolved in 150 c.c. of boiling water and treated with 400 c.c. of alcohol. On keeping, the nitro-compound separated in the amorphous state, but gradually transformed into clusters of microscopic needles (yield, 11·5 g.) (Found in product from 50% alcohol: Loss at 160°, 17·1. $C_{24}H_{15}O_{11}N_3S_2Na_2,7H_2O$ requires H_2O, 16·7%. Found in dried salt: Na, 7·2. $C_{24}H_{15}O_{11}N_3S_2Na_2$ requires Na, 7·3%). This *nitro-compound* is best obtained white and in needles by stirring it with just insufficient boiling water to dissolve it and adding alcohol gradually to complete its solution and then several volumes of alcohol. The *calcium* and *barium* salts are sparingly soluble.

2-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The foregoing nitro-compound (12·0 g.) was dissolved in 222 c.c. of 0·5*N*-sodium hydroxide and reduced with ferrous chloride and alkali at 15° in the usual way. The filtrate and alkaline extracts of the ferric hydroxide were acidified and separation of the anisotropic solid was completed by saturation with sodium chloride. The gelatinous solid obtained on filtration was dissolved in 100 c.c. of boiling water and treated with 300 c.c. of

alcohol. On keeping at 0° for some days, a gelatinous, anisotropic mass filled the fluid. This was collected by filtration and washed free from chloride by 90% alcohol. The mother-liquors were concentrated to a small volume and re-treated in a similar way. The total yield of solid, dried in a vacuum, was 9·0 g. (Found: Loss at 160°, 20·6. $C_{24}H_{18}O_9N_3S_2Na,8\frac{1}{2}H_2O$ requires H_2O, 20·9%. Found in dried salt: Na, 4·3. $C_{24}H_{18}O_9N_3S_2Na$ requires Na, 4·0%). This *amino-compound* is readily soluble in hot water and separates on cooling in gelatinous, anisotropic needles. It is very readily salted out and if such a solution be warmed until clear and be allowed to cool, it sets to a clear anisotropic gel. A dilute solution in hydrochloric acid gives a clear anisotropic, gelatinous solution on addition of sodium nitrite and the product couples with alkaline β-naphthol. Hot dilute nitric acid gives a red coloration, and an alkaline solution couples with diazotised sulphanilic acid with production of an eosin-like coloration.

s-*Carbamide of* 2 : 8-*Aminonaphthol*-3 : 6-*disulphonic Acid*.—2R-Acid (5·0 g.) in 250 c.c. of water containing 26 g. of anhydrous sodium carbonate was phosgenated until the reaction was acid to Congo-paper. The solution was neutralised and saturated with sodium chloride and on being kept for several days deposited the carbamide mixed with some unchanged amine. It was redissolved, submitted to a second phosgenation, and when the conditions were adjusted for its isolation it slowly separated. It crystallised from 2 volumes of boiling water in rods (yield, 45%) (Found: Loss at 160°, 19·2. $C_{21}H_{12}O_{15}N_2S_4Na_4,10H_2O$ requires H_2O, 19·3%. Found in dried salt: Na, 12·3. $C_{21}H_{12}O_{15}N_2S_4Na_4$ requires Na, 12·2%). This *carbamide* is readily soluble in water and is not readily salted out. It gives no precipitate with concentrated hydrochloric acid, whereas 2R-acid gives a precipitate of needles. Unlike 2R-acid, it gives a microcrystalline *barium* salt on addition of concentrated barium chloride solution.

s-*Carbamide of* 2-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The parent amine (5·8 g.) was submitted to a double phosgenation in the usual way. The precipitated solid was dissolved in 17·5 c.c. of boiling water with neutralisation and precipitated by addition of an equal volume of alcohol (yield of material dried in a vacuum, 2·8 g.) (Found: Loss at 160°, 13·6. $C_{35}H_{22}O_{17}N_4S_4Na_4,8\frac{1}{2}H_2O$ requires H_2O, 13·4%. Found in dried solid: Na, 9·2. $C_{35}H_{22}O_{17}N_4S_4Na_4$ requires Na, 9·3%). This *carbamide* is readily soluble in water and crystallises from very concentrated solutions as a microcrystalline powder, but better by addition of sodium chloride. The *calcium* and *barium* salts are sparingly soluble.

s-*Carbamide of* 2-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid.*—The parent amine (5 g.) in 100 volumes of water containing 20 g. of sodium carbonate was submitted to a double phosgenation at 30°. The precipitated solid was neutralised, dissolved in 120 c.c. of boiling water, and treated with 120 c.c. of absolute alcohol. The yield of material dried in a vacuum over sulphuric acid was 3·0 g. (Found: Loss at 160°, 11·9. $C_{49}H_{32}O_{19}N_6S_4Na_4,9H_2O$ requires H_2O, 11·7%. Found in dried solid: Na, 7·6. $C_{49}H_{32}O_{19}N_6S_4Na_4$ requires Na, 7·5%). This *carbamide* is easily soluble in warm water and is readily salted out as a weakly anisotropic solid. Concentrated hydrochloric acid precipitates a weakly anisotropic, finely divided substance, possibly the free tetrasulphonic acid. The *magnesium*, *calcium*, and *barium* salts are sparingly soluble, gelatinous substances.

m-*Nitrobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—The parent naphthylaminetrisulphonic acid (9·0 g. of disodium salt) was nitrobenzoylated in the usual way. After removal of nitrobenzoic acid the neutralised liquors on concentration gave the required amide, which was recrystallised from a small volume of water (yield, 13·55 g.) (Found: Loss at 160°, 11·7. $C_{17}H_9O_{12}N_2S_3Na_3,4\frac{1}{2}H_2O$ requires H_2O, 11·9%. Found in dried substance: Na, 11·4. $C_{17}H_9O_{12}N_2S_3Na_3$ requires Na, 11·5%). This *amide* is very readily soluble in water and is only salted out with difficulty. It is best crystallised from diluted alcohol and then separates in clusters of needles. It forms a readily soluble *calcium* salt and a somewhat less soluble *barium* salt, crystallising in woolly needles.

m-*Aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—13·3 G. of the above nitro-amide were reduced with ferrous chloride and alkali. The neutralised filtrates, freed from iron, were concentrated under reduced pressure at 80° and as much sodium chloride removed as possible by evaporation and filtration and precipitation with alcohol. The amino-compound was then precipitated as an oil by excess of alcohol and gradually solidified. The yield of crude material containing some sodium chloride was 11·1 g. It was not obtained sufficiently pure for analysis. It is extremely soluble in water and is not salted out. It is also soluble in hot methyl alcohol. It diazotises and then couples with β-naphthol. From ethyl-alcoholic solutions containing a little water it crystallises in needles or prisms.

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—8 G. of the above amino-compound were nitrobenzoylated in the usual way. The neutralised liquor on concentration deposited a felted mass of needles, which were collected

without washing, dissolved in 10 c.c. of hot water, and treated with 50 c.c. of alcohol. When cool, the required nitro-amide had separated as a felt of very fine needles (yield, 7·4 g.). For analysis, it was recrystallised from 90% alcohol (Found: Loss at 160°, 16·7. $C_{24}H_{14}O_{13}N_3S_3Na_3,8H_2O$ requires H_2O, 16·7%. Found in dried substance: Na, 9·4. $C_{24}H_{14}O_{13}N_3S_3Na_3$ requires Na, 9·6%). This *nitro-amide* is very easily soluble in water, but is readily salted out. On addition of calcium or barium chloride the *calcium* or *barium* salt is precipitated as a gelatinous, anisotropic product, but on keeping the barium salt crystallises in tufts of woolly needles.

m'-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid*.—The preceding nitro-compound (7·5 g.) was reduced at 0° with ferrous chloride in the usual way. The solution, neutralised to Congo-paper and free from iron, was concentrated to about 60 c.c.; it then set to a paste of fine, short needles. These were collected without washing, dissolved in 20 c.c. of hot water, and treated with 25 c.c. of absolute alcohol. The product separated as an anisotropic, gelatinous mass filling the solution. It was filtered off and well washed with 80% alcohol, but could not thus be freed from chloride. The yield of material dried in a vacuum was 4·5 g. This product is a *disodium* salt and can be salted out from aqueous solutions, but not very readily. For analysis it was dissolved in a small volume of hot water, neutralised to litmus, and treated with several volumes of alcohol. On keeping, the solution deposited balls of woolly needles of the *trisodium* salt (Found in material dried in a vacuum: Loss at 160°, 8·7. $C_{24}H_{16}O_{11}N_3S_3Na_3,3\frac{1}{2}H_2O$ requires H_2O, 8·4%. Found in anhydrous solid: Na, 9·6. $C_{24}H_{16}O_{11}N_3S_3Na_3$ requires Na, 10·0%). The trisodium salt is not salted out and is extremely readily soluble in water. If the reaction of the original liquors from the reduction be neutral to litmus instead of neutral or acid to Congo, no amino-compound separates until almost all the sodium chloride has been removed and the solution concentrated to a syrup.

s-*Carbamide of* 1-*Naphthylamine*-4 : 6 : 8-*trisulphonic Acid*.—The parent amine (10 g.) was phosgenated at 30° in a solution containing 100 g. of anhydrous sodium carbonate in 250 c.c. of water. The solution was neutralised and concentrated repeatedly under reduced pressure with intermediate removal of as much sodium chloride as possible. The residual filtrate was evaporated almost to dryness in a vacuum, treated with a few c.c. of warm water, and decanted from undissolved sodium chloride. On cooling, the carbamide separated in long, delicate needles, which were recrystallised from a little water. In this way, 4·1 g. of the carbamide were obtained, still containing some sodium chloride which could not be removed

from the limited quantities at our disposal. This *carbamide* is extremely readily soluble in water, is not salted out, and gives no precipitate on addition of concentrated hydrochloric acid or alkaline-earth chlorides.

s-*Carbamide of* m-*Aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—The unisolated amino-compound prepared from 10 g. of the corresponding nitro-compound was made up to 500 c.c. with water and treated with 40 g. of anhydrous sodium carbonate, and carbonyl chloride passed in until the solution was acid. The neutralised solution was concentrated and as much sodium chloride removed as possible, first by direct crystallisation, then by addition of ethyl alcohol, and finally by addition of methyl alcohol. The liquor was then concentrated to a small volume and several volumes of methyl alcohol were added so long as there was precipitation of sodium chloride; after a few days, below 0°, the required carbamide separated in soft needles (yield, 6·8 g.). For analysis, it was recrystallised under the same conditions from 66% methyl alcohol at — 5° (Found in material dried in a vacuum : Loss at 160°, 6·1. $C_{35}H_{20}O_{21}N_4S_6Na_6,4H_2O$ requires H_2O, 5·8%. Found in dried solid : Na, 11·4. $C_{35}H_{20}O_{21}N_4S_6Na_6$ requires Na, 11·9%). This *carbamide* is hygroscopic and extremely readily soluble in water or in 98% methyl alcohol and is not salted out.

s-*Carbamide of* m'-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—The base prepared from the nitro-compound (13·8 g. anhydrous) without isolation was phosgenated in 500 c.c. of water in presence of 50 g. of anhydrous sodium carbonate. The carbamide was isolated in the same way as the preceding member. The yield of crystalline solid containing a little chloride was 9·65 g. For analysis, it was dissolved in 10 c.c. of hot water and treated with 35 c.c. of 98% methyl alcohol; it then slowly crystallised, below 0°, in clusters of white needles. It was washed with 80% methyl alcohol, cooled to — 5° (yield, 8·1 g.). As it was hygroscopic, it was dried in a vacuum (Found : Loss at 160°, 9·3. $C_{49}H_{30}O_{23}N_6S_6Na_6,8H_2O$ requires H_2O, 9·3%. Found in dried solid : Na, 9·5. $C_{49}H_{30}O_{23}N_6S_6Na_6$ requires Na, 9·8%). This *carbamide* is very soluble in water or methyl alcohol and is not salted out. With saturated barium chloride solution, it gives after some delay a *barium* salt in anisotropic particles. It gives no precipitate with lead acetate, but is precipitated by basic lead acetate.

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CCCCVIII.—*Investigations on the Reactivity of Halogens in Various Types of Naphthalene Derivatives. Part I.*

By JOHN BALDWIN SHOESMITH and HANNES RUBLI.

A SERIES of investigations has been undertaken with the view of extending work already carried out on halogenated derivatives of benzene (J., 1922, **121**, 1391; 1923, **123**, 2828; 1924, **125**, 1312, 2278; 1926, 214, 2832; this vol., p. 1768) to the naphthalene series. It has been discovered that the ease of replacement of both nuclear and side-chain halogen in naphthalene compounds is markedly different from that in the corresponding benzene derivatives; thus, α- and β-naphthylmethyl bromides are both more readily hydrolysed in aqueous alcohol at 25° than is benzyl bromide, the order of ease of hydrolysis being $\alpha > \beta$, a fact which substantiates the rule put forward by Olivier (*Rec. trav. chim.*, 1923, **42**, 775) showing the connexion between the rate of hydrolysis of benzyl halides and substitution in the aromatic nucleus. Owing to the rapidity of the hydrolysis, it was not possible to ascertain whether this order remained the same at higher temperatures, but it appeared to be so at 60°. The two isomerides are also almost equally more rapidly reduced than benzyl bromide at 77°.

Of the α- and β-bromo- and iodo-naphthalenes, only α-iodonaphthalene is appreciably reduced at 100° by hydrogen iodide, and it appears as if the halogen (especially iodine) attached to the nucleus in the position which is most readily attacked during substitution is correspondingly most readily removed by hydrogen iodide.

The reduction of 1-bromo-β-naphthol and 4-bromo-α-naphthol proved of interest in that (1) they are both very readily reduced, and (2) the order of ease of reduction is $o > p$, the reverse of the case in the corresponding benzene series. It has already been suggested (J., 1924, **125**, 1314) by one of us, and independently by Nicholet (*J. Amer. Chem. Soc.*, 1927, **49**, 1812), that the intermediate formation of molecules of a quinonoid type probably assists the reduction of such compounds, a suggestion borne out by the great reactivity of the ortho-compound above (since ortho-quinonoid forms are recognised as more prevalent in the naphthalene than in the benzene series), and also by the very slow rate of reduction of 5-bromo-α-naphthol in which the possibility of intervention of quinonoid formation is not so marked.

The formation of active quinonoid molecules is probably a powerful factor in the ease of reduction of the second series of nuclear-

halogenated naphthalene derivatives examined,* *viz.*, 1-bromo-2-methylnaphthalene and 4-bromo-1-methylnaphthalene, both of which are reduced by hydriodic acid at 100°, in contradistinction to the bromotoluenes, which are stable, and the order is again 1 : 2 > 1 : 4.

In various substituted α-naphthylmethyl bromides the reactivity of the bromine atoms was in the decreasing order *p*-OMe > *p*-CH_3 > unsubs. > *p*-Br, which is the same as in the hydrolysis of substituted benzyl bromides, the reciprocal of the time (in days) for 50% hydrolysis, which gives a measure of the velocity coefficient, being shown in parenthesis after each compound : *4-methoxy-α-naphthylmethyl bromide*(∞) > *4-methyl-α-naphthylmethyl bromide* (6·0) > α-naphthylmethyl bromide (0·55) > 4-bromo-α-naphthylmethyl bromide (0·29). 4-Methoxy-α-naphthylmethyl bromide resembles *p*-methoxybenzyl bromide in being almost instantaneously hydrolysed in aqueous alcohol, and its great reactivity, *e.g.*, in a moist atmosphere (see Experimental), must be due to the combined influences of the general and the powerful alternating effect of the methoxyl group, supplemented by a further effect due to the compound's "naphthalenoid" (as opposed to benzenoid) character. 4-Methyl-α-naphthylmethyl bromide also is very readily hydrolysed in aqueous alcohol, and the naphthalenoid enhancing influence is so great that in 2-methyl-α-naphthylmethyl bromide, in which a decreased reactivity might have been expected from steric hindrance, the bromine atom is almost as readily replaced as that in the 1 : 4-isomeride.

Whilst the hydrolysis of the methoxyl and methyl compounds proved to be too rapid to allow a satisfactory velocity coefficient to be obtained, the comparative slowness of the hydrolysis of the unsubstituted α- and β-naphthylmethyl bromides and of 4-bromo-α- and 1-bromo-β-naphthylmethyl bromides has enabled us to obtain a

TABLE I.

Compound.	$k \times 10^6$.	Compound.	$k \times 10^6$.
1. $C_{10}H_7 \cdot CH_2Br(\alpha)$	270	6. $Br(4) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$ ...	137
2. $C_{10}H_7 \cdot CH_2Br(\beta)$	210	7. $Br(1) \cdot C_{10}H_6 \cdot CH_2Br(\beta)$ ...	59
3. $C_6H_5 \cdot CH_2Br$	125	8. $Br(4) \cdot C_6H_4 \cdot CH_2Br(1)$ ...	71
4. $MeO(5) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$	485	9. $Br(2) \cdot C_6H_4 \cdot CH_2Br(1)$ ...	39
5. $Br(5) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$ ...	129		

numerical value of the increased reactivity, due to the compounds having acquired naphthalenoid characteristics in the α or β-position, by comparing the values in Table I (k = unimolecular velocity

* That formation of molecules of a quinonoid type might be intermediate in the reduction of the halogenated methylnaphthalenes appears probable in view of recent work of Schorigin (*Ber.*, 1926, **59**, 2504), who claims to have demonstrated the existence of the quinonoid modification of toluene.

coefficient at 25°). The ratio for compounds 1 and 3 is 2·16, and that for compounds 6 and 8 is 1·92; the reaction is therefore approximately twice as fast for the α-naphthalene derivatives as for the corresponding benzene derivatives. In the case of the β-naphthalene derivatives the increase is not so great, as may be seen from the ratio between Nos. 2 and 3 (1·68) and between Nos. 7 and 9 (1·52).

Definite evidence of the transmission of an influence from the 5- to the 1-position of the naphthalene nucleus has been obtained, in that the order of ease of hydrolysis of the following compounds is: *5-methoxy-α-naphthylmethyl bromide* ($k = 0{\cdot}000485$) > α-naphthylmethyl bromide ($k = 0{\cdot}000270$) > *5-bromo-α-naphthylmethyl bromide* ($k = 0{\cdot}000129$); it is important to note that this is the order of reactivity of the 1 : 4-isomerides, but whilst 4-methoxy-α-naphthylmethyl bromide is hydrolysed with great rapidity in aqueous-alcoholic solution, the 1 : 5-isomeride is comparatively slowly hydrolysed. This is in agreement with the generalisation of Olivier (*loc. cit.*), since α-naphthol in the form of its carbonate is brominated in the 4-position. The fact that the 5-methoxy-derivative is more reactive than the unsubstituted compound is of interest, and it is possible that in α-naphthol itself the 5-position is liable to attack, but the overwhelming reactivity of the 4-position completely masks the tendency to produce a 1 : 5-derivative.

The nuclear bromine atom in 5-bromo-α-naphthylmethyl bromide exercises a powerful retarding influence on the rate of hydrolysis of the lateral bromine atom, and the 1 : 4-isomeride ($k = 0{\cdot}000137$) is slightly but definitely more reactive than the 1 : 5-isomeride ($k = 0{\cdot}000129$), which is again in agreement with the production of more 1 : 4-dibromo- than 1 : 5-dibromo-naphthalene in the bromination of α-bromonaphthalene (Armstrong and Rossiter, *Chem. News*, 1892, **65**, 59).

The differences which exist between the hydrolysis of the 1 : 4- and 1 : 5-isomerides suggest that, whilst both alternating and general influences are readily transmitted from the 4- to the 1-position in naphthalene as in the corresponding benzene derivatives, the alternating influence does not readily pass from the 5- to the 1-position. An effect due to the general influence is apparent, *viz.*, the retarded reactivity of 5-bromo-α-naphthylmethyl bromide and the slightly enhanced reactivity of 5-methoxy-α-naphthylmethyl bromide as compared with the unsubstituted α-naphthylmethyl bromide, since bromine retards and methoxyl increases such reactivity in a general way (compare Shoesmith and Slater, J., 1926, 217).

EXPERIMENTAL.

The isomeric naphthylmethyl bromides were prepared by brominating the appropriate methylnaphthalene at the boiling point in direct sunlight. They were purified by crystallisation from alcohol; the α-isomeride had m. p. 53°, and the β- had m. p. 56°. They both possess lachrymatory properties, and produce a burning sensation on the skin.

4-Methoxy-α-naphthylmethyl Bromide.—4-Methoxy-α-naphthaldehyde, prepared from α-naphthyl methyl ether by Gattermann's method (*Annalen*, 1907, **357**, 365), was converted into 4-methoxy-α-naphthylcarbinol of m. p. 35° (*Anal. Fis. Quím.*, 1919, **17**, 125) by means of 66% aqueous potassium hydroxide (25% alcoholic potassium hydroxide was without action), and the carbinol, dissolved in dry benzene, was converted into the corresponding bromide by means of dry hydrogen bromide. The resulting yellow needles could not be recrystallised from any solvent owing to their great instability; they had m. p. 119—120° (decomp.) (Found: Br, hydrolysable, 24·7. $C_{12}H_{11}OBr,C_6H_6$ requires Br, 24·3%). The whole of this bromine became ionisable in 90% aqueous alcohol in 5 minutes. The yellow crystals fumed and rapidly liquefied in the atmosphere owing to hydrolysis.

An attempt to prepare 2-methoxy-α-naphthylcarbinol by a similar method was unsuccessful; 4-methoxy- and 2-methoxy-α-naphthoamides were found by Gattermann (*Annalen*, 1888, **244**, 72) to display analogous differences in their behaviour with potassium hydroxide; moreover 2-methoxy-α-naphthaldehyde gives anomalous results with Schiff's reagent. An attempt to obtain the carbinol by reduction of 2-methoxy-α-naphthaldoxime (by means of sodium amalgam in glacial acetic acid) to the corresponding amine also failed. This suggests that reactions involving the carbon atom of the aldehyde group are inhibited by the proximity of the methoxyl group on the one side and the additional ring system on the other.

An attempt was also made to prepare 3-methoxy-α-naphthylmethyl bromide, and the synthesis was carried as far as the corresponding alcohol, but insufficient of this was obtained for the purpose.

3-Methoxy-α-naphthaldehyde.—α-Naphthylamine-3 : 8-disulphonic acid (100 g.), dissolved in 1 l. of water containing 25 g. of sodium hydroxide, was reduced with 200 g. of 4% sodium amalgam, and the α-naphthylamine-3-sulphonic acid was converted into *3-methoxy-α-naphthaldehyde* by the methods already given (J., 1926, 3241). Especial care was necessary to ensure the absence of 3-hydroxy-α-naphthoic acid from the intermediate 3-methoxy-α-naphthoic acid; this was converted into *3-methoxy-α-naphthoyl chloride*, yellow

needles from light petroleum, m. p. 79° (Found: Cl, 15·5. $C_{12}H_9O_2Cl$ requires Cl, 16·1%), which was catalytically reduced. The aldehyde crystallises from light petroleum in colourless, rhombic plates, m. p. 60° (Found: C, 77·1; H, 5·4. $C_{12}H_{10}O_2$ requires C, 77·5; H, 5·4%); *oxime*, white needles from aqueous alcohol, m. p. 102°; p-*nitrophenylhydrazone*, brick-red needles from acetic acid, m. p. 197°; *semicarbazone*, white needles from aqueous alcohol, m. p. 200°. The yield of aldehyde is very small and only sufficient was obtained for characterisation and conversion as above into a small sample of 3-*methoxy-α-naphthylcarbinol*. The carbinol crystallised from water in fine, colourless needles, m. p. 88° (Found: C, 76·1; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%).

4-Bromo-α-naphthol was prepared by Reverdin and Kauffmann's method (*Ber.*, 1895, **28**, 3053) and, when purified by steam distillation in an atmosphere of nitrogen, was obtained as colourless needles, m. p. 129°. When the intermediate 4-bromo-α-naphthyl carbonate is treated in methyl-alcoholic solution alternately with 5% methyl-alcoholic potassium hydroxide and methyl sulphate in an atmosphere of nitrogen, *4-bromo-α-naphthyl methyl ether*, a colourless oil, b. p. 181°/18 mm. (Found: Br, 33·6. $C_{11}H_9OBr$ requires Br, 33·8%), may be obtained.

1-Bromo-β-naphthol, prepared by direct bromination of β-naphthol and repeatedly crystallised from acetic acid, had m. p. 84°.

1-Bromo-β- and 4-bromo-α-methylnaphthalenes were prepared by direct bromination of β- and α-methylnaphthalene, respectively, and purified by repeated fractionation in a vacuum. The samples used in the reduction experiments were free from hydrolysable bromine. They were converted into 1-bromo-β-naphthylmethyl bromide (m. p. 107°) and 4-bromo-α-naphthylmethyl bromide (m. p. 103°), respectively, by a current of dry bromine at 210—220°, and recrystallisation from light petroleum (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839).

4-Methyl-α-naphthylmethyl Bromide.—4-Bromo-1-methylnaphthalene (13 g.) was treated in ethereal solution with magnesium (1·5 g.), and after the vigorous reaction had ceased paraformaldehyde (18 g.) was added, and the whole heated for 48 hours; the product was mixed with ice and sulphuric acid, extracted with ether, the ether evaporated, the residual oil dissolved in alcohol, and the 4-methyl-α-naphthylcarbinol, m. p. 75°, obtained by fractionally precipitating the oil first with water. The carbinol was converted into *4-methyl-α-naphthylmethyl bromide* in dry benzene by means of hydrogen bromide. It crystallised from light petroleum in long needles, m. p. 77° (Found: Br, 34·3. $C_{12}H_{11}Br$ requires Br, 34·0%).

2-Methyl-α-naphthylmethyl bromide was obtained similarly

from 1-bromo-2-methylnaphthalene, and had m. p. 88° (Ziegler and Tiemann, *Ber.*, 1922, **55**, 3411).

For comparative purposes, ω-bromo-*p*-xylene was prepared from *p*-toluonitrile by reduction by Stephen's method (J., 1925, **127**, 1874) to *p*-tolualdehyde, and thence by 25% alcoholic potassium hydroxide to *p*-tolylcarbinol, which gave ω-bromo-*p*-xylene on treatment with hydrogen bromide. This should also prove a more convenient method for the preparation of the meta-isomeride than any yet published.

Attempts to prepare 4-bromo-2-methylnaphthalene were without appreciable success; the method of Vesely and Kapp (*Rec. trav. chim.*, 1925, **44**, 371) failed to produce a satisfactory yield of the required 4-amino-2-methylnaphthalene, and a method involving the bromination of aceto-2-methyl-α-naphthalide with subsequent elimination of the amino-group yielded only a trace of impure 4-bromo-2-methylnaphthalene.

Aceto-4-bromo-2-methyl-α-naphthalide.—Aceto-2-methyl-1-naphthalide (Lesser, *Annalen*, 1913, **402**, 38) (5 g.) was dissolved in 25 c.c. of glacial acetic acid, and bromine (5 g.) in glacial acetic acid (3 c.c.) slowly added. After 1 hour, the mixture was poured into water; the precipitate obtained crystallised from alcohol in flocculent needles, m. p. 223° (Found: Br, 28·7. $C_{13}H_{12}ONBr$ requires Br, 28·8%). This acetyl derivative was hydrolysed by a boiling mixture of hydrochloric acid (8 parts) and alcohol (8 parts). After 6 hours, the whole was poured into water, and concentrated ammonia added to the hot solution. The precipitated *4-bromo-2-methyl-α-naphthylamine* crystallised from light petroleum in white needles (rapidly becoming pink in the air), m. p. 82° (Found: Br, 33·4. $C_{11}H_{10}NBr$ requires Br, 33·9%); the yield was very poor.

5-Bromo-α-naphthylmethyl Bromide.—The bromination of α-naphthoic acid dissolved in warm glacial acetic acid produced 5-bromo-α-naphthoic acid, which, when recrystallised several times from alcohol, had m. p. 262° (Found: Br, 31·5. Calc.: Br, 31·8%) (Eckstrand, *J. pr. Chem.*, 1888, **38**, 155, gives m. p. 246°; Raiford and Lankelma, *J. Amer. Chem. Soc.*, 1925, **47**, 1119, give 244°). The acid was converted by means of thionyl chloride into 5-bromo-α-naphthoyl chloride (compare Raiford and Lankelma, *loc. cit.*); this was recrystallised from light petroleum (b. p. 40—60°), and reduced by Rosenmund's method (*Ber.*, 1918, **51**, 591) to 5-bromo-α-naphthaldehyde (see Rupe and Metzger, *Helv. Chim. Acta*, 1925, **8**, 838), which crystallised from light petroleum in white, prismatic needles, m. p. 104° (Found: Br, 33·9. Calc.: Br, 34·1%); *p-nitrophenylhydrazone*, red needles from acetic acid, m. p. 263°. The aldehyde was allowed to stand in contact with twice

its weight of 66% aqueous potassium hydroxide and a few drops of alcohol for 3 days, being warmed for a few minutes each day to 60°. When reduction was considered to be complete, the reaction mixture was diluted with water and extracted with ether, the extract shaken with sodium bisulphite solution to remove unchanged aldehyde, and the ether evaporated. The *5-bromo-α-naphthylcarbinol* so obtained crystallised from light petroleum as fine, white needles, m. p. 124° (Found: C, 55·5; H, 3·7. $C_{11}H_9OBr$ requires C, 55·7; H, 3·8%). Dry hydrogen bromide passed into the benzene solution of this gave *5-bromo-α-naphthylmethyl bromide*, which crystallised from light petroleum in white needles, m. p. 101° (Found: Br, hydrolysable, 26·7. $C_{11}H_8Br_2$ requires Br, hydrolysable, 26·8%).

5-Methoxy-α-naphthylmethyl Bromide.—5-Methoxy-α-naphthaldehyde (Shoesmith and Rubli, J., 1926, 3241) was prepared in a relatively large quantity (5 g.). The purification of 5-methoxy-α-naphthoic acid was more economically effected by repeated crystallisation than by our former method, and Dr. C. E. Sosson has obtained a sample of m. p. 230°. The corresponding acid chloride, obtained by the use of thionyl chloride, yields the aldehyde on reduction (yield, 30—40%).

The aldehyde was reduced as in the case of the bromo-compound above; the *5-methoxy-α-naphthylcarbinol* obtained crystallised from water in long, colourless needles, m. p. 98° (Found: C, 76·5; H, 6·3. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%); with dry hydrogen bromide in benzene solution it yielded *5-methoxy-α-naphthylmethyl bromide*, which crystallised from light petroleum (b. p. 40—60°) in white, prismatic needles, m. p. 65° (Found: Br, 31·4. $C_{12}H_{11}OBr$ requires Br, 31·9%). It is more stable in the air than the 4-methoxy-derivative. Both 5-bromo- and 5-methoxy-α-naphthylmethyl bromides produce a burning sensation on the skin, but neither is lachrymatory.

5-Bromo-α-naphthol.—Bromine (40 g.) was gradually dropped into vigorously stirred, *dry*, molten α-nitronaphthalene (85 g.), the temperature being maintained at 80—100°. 5-Bromo-α-nitronaphthalene, m. p. 122°, was obtained pure by crystallising the reaction mixture from alcohol, and was reduced by West's method (J., 1925, **127**, 994) to 5-bromo-α-naphthylamine, which crystallised from ligroin in plates, m. p. 69°. The insoluble sulphate of this compound was diazotised in the usual manner. The rather stable diazonium sulphate decomposed most satisfactorily when dropped into a boiling solution of 43% sulphuric acid; 5-bromo-α-naphthol was then distilled in steam, and crystallised as white needles, m. p. 137° (Fuson, *J. Amer. Chem. Soc.*, 1924, **46**, 2779).

Hydrolysis of Compounds containing Halogen in the Side Chain.—The hydrolyses were carried out at 25° in aqueous alcohol prepared by the addition of sufficient alcohol to every 10 c.c. of water to produce a volume of 100 c.c., 10 c.c. of the reagent being used for each 0·06 (approx.) g. of compound. Aliquot portions of the mixture were at intervals run into a large excess of water and rapidly titrated with standard alkali. The resulting unimolecular velocity coefficient, k (Table I), was satisfactorily constant in each case.

The rapidity of hydrolysis of 4-methyl-α-naphthylmethyl bromide (A) and 2-methyl-α-naphthylmethyl bromide (B) is seen from Table II, in which the hydrolysis of 4-bromo-α-naphthylmethyl bromide (C) is included for comparison, and t, w, and x have the same significance as in former publications.

TABLE II.

	A.	B.		C.
w =	0·5172	0·5080		0·6125
t (hours).	x.	x.	t (days).	x.
2	29	24	2	32·4
4	50	45	3	44·8
8	68	65	4	54·7
25	95	94	7	75·1

TABLE III.

	Reagent.				
Compound.	$C_2H_4O_2$ (c.c.).	HI (c.c.).	T.	t (hrs.).	x.
$C_{10}H_7Br(\alpha)$	10	10	100°	4	4
$C_{10}H_7Br(\beta)$	,,	,,	,,	,,	Nil
$C_{10}H_7I(\alpha)$	,,	,,	,,	,,	62
$C_{10}H_7I(\beta)$	,,	,,	,,	,,	7
$C_{10}H_7\cdot CH_2Br(\alpha)$ ...	,,	,,	,,	1	96
,, ...	,,	,,	77	2	40
,, ...	,,	,,	,,	4	65
$C_{10}H_7\cdot CH_2Br(\beta)$ ...	,,	,,	100	1	96
,, ...	,,	,,	77	2	42
,, ...	,,	,,	,,	4	71
$Br(1)\cdot C_{10}H_6\cdot OH(\beta)$	15	5	,,	0·25	94*
,,	22	,,	25	0·50	63
,,	,,	,,	,,	0·75	76
,,	,,	,,	,,	1·50	93
$Br(4)\cdot C_{10}H_6\cdot OH(\alpha)$	15	,,	77	0·25	95*
,,	22	,,	25	0·50	27
,,	,,	,,	,,	0·75	38
,,	,,	,,	,,	1·50	63
$Br(1)\cdot C_{10}H_6\cdot CH_3(\beta)$	10	,,	100	2	60
,,	,,	,,	,,	4	78
,,	,,	,,	,,	6	88
$Br(4)\cdot C_{10}H_6\cdot CH_3(\alpha)$	,,	,,	,,	2	29
,,	,,	,,	,,	4	50
,,	,,	,,	,,	6	62
$Br(5)\cdot C_{10}H_6\cdot OH(\alpha)$	,,	,,	,,	5	20

* The ease of reduction of these compounds is indicated here.

The reciprocal of the time (in days) taken for half hydrolysis of ω-bromo-*p*-xylene was 1·0.

Reduction of Various Halogenated Naphthalene Derivatives.—In Table III are summarised all the results of the reduction experiments with hydriodic acid. These were carried out in the usual manner, approximately 0·170 g. of each compound being used in glacial acetic acid and constant-boiling hydriodic acid; t and x have their usual significance, whilst T is the temperature of experiment. The liberated iodine in each case was taken as a measure of the amount of reduction which had taken place.

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EDINBURGH UNIVERSITY. [*Received, October 3rd*, 1927.]

CCCCIX.—*Investigation of the Constitution of Glycerides in Natural Fats. A Preliminary Outline of Two New Methods.*

By THOMAS PERCY HILDITCH and COLIN HENRY LEA.

QUANTITATIVE information in regard to the composition of the natural fats is much less available than in the case of most natural organic materials. It is only within the past few years that trustworthy data have been forthcoming as to the quantitative composition of the fatty acids present in combination in natural fats, and even at the present time the fats for which such figures are available form but a small proportion of the total number of those in common use. Information as to the manner in which these fatty acids are combined with glycerol in the natural fats is still more lacking, and it is indeed no exaggeration to say that at present we are without anything approaching quantitative knowledge of the structure of the glycerides in any of the natural fats.

The qualitative detection of individual solid glycerides by subjecting natural fats to exhaustive crystallisation from selected solvents has received much attention by several investigators, for example, Klimont (*Monatsh.*, 1902, **23**, 51; 1903, **24**, 408; 1904, **24**, 929; 1905, **26**, 563; 1912, **33**, 441; etc.), Bömer (*Z. Unters. Nahr. Genussm.*, 1907, **14**, 90; 1909, **17**, 353; 1913, **25**, 321; 1920, **40**, 97; 1924, **47**, 61; etc.) and Amberger (*ibid.*, 1913, **26**, 65; 1918, **35**, 313; 1923, **46**, 276, 291; 1924, **48**, 371; etc.); as Klimont

has emphasised, it is difficult (if not impossible) to obtain complete separation of any one component by this procedure.

The present communication is a description of the results so far obtained in some attempts to attack this complex problem by the application of new principles. We are not yet in a position to give a complete analysis of all the glycerides composing any natural fat, but there is reason to believe that further progress along the lines of investigation which we have developed will lead to more complete results in this direction. Many of the products which result from our treatment of the fats are novel in type, and new methods of separation must perforce be devised as the work develops; it is therefore probable that complete execution of the scheme we have in mind will occupy considerable time. Our procedure, however, now permits us to ascertain for the first time the proportion of completely saturated triglycerides present in a fat, and also to suggest certain general features of the structure of natural fats which have already become apparent.

General Description of the Methods employed.—The primary objective has been to alter the chemical characteristics of the glycerides in such a way that, without disturbance of the combined glyceryl radical, new glycerides may be formed which are separable more readily than the original natural mixture.

Two methods have been applied for this purpose, both of them processes of controlled oxidation which have been applied hitherto to the simple esters of the higher unsaturated fatty acids:

1. E. F. Armstrong and one of us (*J. Soc. Chem. Ind.*, 1925, **44**, 43T) showed that the methyl or ethyl ester of a higher unsaturated fatty acid, when dissolved in acetone and submitted to the action of powdered potassium permanganate, broke down almost quantitatively into a monobasic fatty acid and the hydrogen ester of a dicarboxylic acid:

$$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Me \longrightarrow CH_3\cdot[CH_2]_7\cdot CO_2H + HO_2C\cdot[CH_2]_7\cdot CO_2Me.$$

We have now found that the same decomposition can be effected in the case of neutral glycerides without appreciable rupture of the glyceryl ester-linking. In cases where the unsaturated glycerides are derived from either oleic, linoleic or linolenic acid, the products of oxidation are, in addition to nonoic, hexoic or propionic acid, complex glycerides united to at least one azelaic acid residue (the remaining carboxyl group of which is free). If the possible combinations of glycerol with saturated fatty acid ($S\cdot CO_2H$) and oleic acid ($U\cdot CO_2H$) be considered, it will be seen that the following products may arise:—

	Original glyceride.	Product of oxidation.
Fully saturated	$C_3H_5(O{\cdot}CO{\cdot}S)_3$	$C_3H_5(O{\cdot}CO{\cdot}S)_3$
Mono-oleo-derivative ...	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)_2\\(O{\cdot}CO{\cdot}U)\end{cases}$	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)_2\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H)\end{cases}$
Dioleo-derivative	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)\\(O{\cdot}CO{\cdot}U)_2\end{cases}$	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H)_2\end{cases}$
Triolein	$C_3H_5(O{\cdot}CO{\cdot}U)_3$	$C_3H_5(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H)_3$

The acid azelaic glycerides (of which it is necessary in due course to synthesise individual representative members, in order to study and compare their characteristics) form as a rule a somewhat complicated mixture, difficult at present to separate satisfactorily. Only general discussion of these products is therefore offered at the moment, and their detailed examination is reserved for a future communication: methods for quantitative separation of the total neutral products (*i.e.*, completely saturated glycerides) from the acidic products of oxidation (emanating from any glycerides containing unsaturated fatty acids) are, however, given.

2. It was found by one of us (J., 1926, 1828) that hydrogen peroxide in concentrated acetic acid solution effected the practically complete conversion of oleic acid or of methyl oleate into a corresponding dihydroxystearic derivative. The dihydroxystearic compounds are in general distinguished from the simply fatty acids by their higher melting points and sparing solubility in most solvents, and it was thought that similar treatment of the natural fats might convert them into mixtures more amenable to fractional crystallisation than the original materials. The products to be expected may be given as follows:—

Glyceride.	Product.
Fully saturated	$C_3H_5(O{\cdot}CO{\cdot}S)_3$
Mono-oleo-derivative	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)_2\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CH_3)\end{cases}$
Dioleo-derivative	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CH_3)_2\end{cases}$
Triolein	$C_3H_5(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CH_3)_3$

This method has not, up to the present, yielded results quite so promising as the more disruptive oxidation, partly in consequence of complications in the mode of addition of the hydroxyl radicals to the ethylenic linkage which escaped notice in the earlier work on the action of hydrogen peroxide upon oleic acid or its simple esters (compare Experimental, p. 3114). Nevertheless, the unsaturated glycerides can be converted completely into dihydroxylated deriv-

atives by this procedure and its employment in conjunction with the other method has assisted us in formulating the conclusions now put forward.

Discussion of the Results obtained.—We shall refer mainly in this paper to the data which we have collected on the constitution of the glycerides of mutton tallow, cacao butter, and cotton-seed oil. We hope at a later stage to report in fuller detail upon the constitution of individual fats (in addition to the above, fats such as lard, palm-kernel oil, palm oil, Chinese vegetable tallow, Illipé fat, and other vegetable and animal fats are included in the scheme of investigation by these methods in these laboratories), but we desire here to draw comparisons between different types of fat rather than to deal with individual cases.

The composition of the fatty acids combined in mutton tallow, cacao butter and cotton-seed oil is given by Armstrong and Allan (*J. Soc. Chem. Ind.*, 1924, **43**, 216T) as :

	Mutton tallow.	Cacao butter.	Cotton-seed oil.
Myristic	1·5	—	—
Palmitic	21·0	23·2	23·4
Stearic	30·0	33·6	—
Oleic	43·0	41·8	23·0
Linoleic	5·0	1·4	53·6

We may add that the fatty acids of the cacao butter used in the present experiments gave, on separation and fractional distillation of the methyl esters of the saturated and the unsaturated portions, figures in good general agreement with the above : Palmitic 24·3, stearic 34·5, oleic 39·2, linoleic 2·0.

By applying the permanganate–acetone process of oxidation to these fats, we have obtained the following figures for the percentage of completely saturated glycerides present in the original fat; the results of two separate oxidations are given in each case :

	Completely saturated glycerides, %.	Mean equivalent of fatty acids.
Mutton tallow	24·7	268·2
	26·2	266·5
Cacao butter	Below 5 *	275·4
	4·8	—
Cotton-seed oil	1·6 *	—
	1·5	—

* These figures represent maximum, rather than absolute, percentages present.

The non-volatile acidic products of oxidation, as already mentioned, are low-melting materials the complete separation of which may require considerable time; and we therefore limit discussion for the time being to the general relations disclosed between the

distribution of saturated and unsaturated fatty acids in the glycerides of vegetable and animal fats.

In mutton tallow, which contains 26% of completely saturated glycerides, the fatty acids of which have a mean equivalent of 266·5, we see that, to a first approximation, the proportions of fatty acids in the unsaturated glycerides are, by difference, about 35% of saturated and 65% of unsaturated acids.

On the other hand, the relative composition of the unsaturated glycerides of cacao butter, allowing for 5% of fully saturated glycerides (p. 3109), is about 56·5% of saturated fatty acids and 43·5% of unsaturated fatty acids.

The mean composition of the unsaturated glycerides lies in each case between that of a mono-oleic and that of a dioleic glyceride, but clearly approximates more closely to the former in cacao butter and to the latter in tallow.

So far as cacao butter is concerned, indeed, there is evidence that the predominating components are mono-oleic derivatives, and that oleopalmitostearin is an important constituent. In one of the oxidations carried out as described on p. 3112, the separation of a considerable quantity of an insoluble soap-like mass was observed at the interface between the ethereal solution and the aqueous sodium carbonate. This material was separated by filtration, washed with ether, and then acidified in the usual manner; a hard fatty substance was then obtained which possessed a saponification equivalent of 191 and an equivalent by direct titration of 703 (oleopalmitostearin requires respectively 191·5 and 766); the amount isolated in this manner (which is from the nature of the case not likely to be the whole of that present) was 60% of the total acidic glycerides produced.

The alternative method of oxidation of cacao butter in acetic acid solution with hydrogen peroxide leads to much the same conclusion. Large amounts of apparently homogeneous material, either in the form of dihydroxylated glyceride or as the monoacetyl derivative of the latter (compare p. 3114), were obtained; the products approximated in composition to glycerides containing palmitic, stearic, and dihydroxystearic acids in proportions corresponding closely with those of the palmitic, stearic, and oleic acids present in the original fat.

Whilst dioleo-derivatives are of course present to a certain extent in cacao butter, we are definitely led from our experience with both methods of oxidation to conclude that mono-oleo-derivatives predominate, and there is considerable evidence that oleopalmitostearin is an important component of the fat. This conclusion is not incompatible with Klimont's results (*loc. cit.*), but is not in

accordance with those of Amberger and Bauch (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 371).*

It has been customary in some quarters to conclude that those vegetable fats (of which cacao butter is a notable example) which combine the especially useful qualities of non-greasy, brittle texture and low melting point owe these properties to the presence of certain selectively produced glycerides, and the impression is widely held that certain plants tend to elaborate specific types of glyceride. Our investigations, so far, have led to a somewhat different conclusion, namely, that the fatty acids in vegetable glycerides are distributed impartially rather than selectively, and that there is a distinct tendency towards even distribution of unsaturated acids throughout the whole fat, so that the occurrence of simple triglycerides, and even of mixed saturated glycerides, is reduced to a minimum. If this be the case, the physical properties of a mature vegetable fat depend primarily upon the mixture of fatty acids from which it emanates.

Hence, in the case of cacao butter, in which the proportions of palmitic, stearic and oleic acids approach equality relatively more closely than in most fats, it is not unnatural that the final mixture resembles an individual glyceride in properties more nearly than a fat in which the variation in kind and proportion of the component fatty acids is more pronounced.

Again, permanganate–acetone oxidation of cotton-seed oil has proved that entirely saturated glycerides are present only in very small proportion, although 25% of the combined fatty acids is palmitic acid; this acid is thus practically wholly in combination as mixed glycerides with the unsaturated fatty acids, which in this oil are present in the proportion of about three molecules per molecule of palmitic acid.

Also, work on palm-kernel oil, at present in an early stage in these laboratories, has already indicated that the oleic acid present is combined almost entirely with saturated fatty acids in mono- or di-oleic glycerides.

The only animal fat yet studied by these methods, mutton tallow, has yielded data which point to an entirely different state of affairs, the amount of fully saturated glycerides present being far larger than that in the vegetable fats. We prefer, naturally, to defer further discussion of the animal fats until we have collected a wider range of analytical data.

* These authors state that cacao butter contains 55% of palmitodiolein, 25% of oleodistearin, and 20% of oleopalmitostearin; the calculated iodine value of the original fat is thus 45·7, whereas the recorded figure is 38·6.

EXPERIMENTAL.

I. *Oxidation of Glycerides with Potassium Permanganate in Acetone Solution.*—The fats employed were of best edible quality and were submitted to oxidation in the neutral condition, *i.e.*, after removal of free fatty acids by washing with dilute aqueous alkali.

The procedure employed in working up the products of oxidation differed somewhat in detail with the various fats oxidised, but a typical experiment with mutton tallow may be described.

Mutton tallow. The tallow (100 g.) was dissolved in anhydrous acetone (1000 c.c.), and powdered potassium permanganate (250 g.) added in small quantities with frequent shaking; the heat of reaction was sufficient to keep the acetone in vigorous ebullition (reflux condenser). The mixture was refluxed for 4 hours and kept overnight. (The admixture of sufficient anhydrous magnesium sulphate with the permanganate to neutralise potassium hydroxide liberated during oxidation is a further precaution which we have employed in some cases in order to restrain any tendency to glyceride saponification.) The acetone was distilled off and the residue after admixture with water was treated with sodium hydrogen sulphite and 30% sulphuric acid (the slightest possible excess of free sulphuric acid being maintained) at a moderate temperature until decolorised. The product was extracted several times with somewhat large quantities of ether. In the particular experiment described, the first ethereal extract deposited on standing a white, crystalline solid, which was recrystallised from acetone (A). The combined ethereal extracts were washed free from mineral acid, evaporated to dryness, and combined with the residue from the acetone mother-liquor of (A). This product was dissolved in a little hot alcohol and titrated against *N*-alcoholic potash; the neutralised solution was now poured into aqueous sodium carbonate and extracted repeatedly with ether to remove neutral matter.

The acidic glyceride products of oxidation are not removed efficiently by simple agitation of the ethereal solution with aqueous sodium carbonate, and as an alternative to the potash neutralisation process outlined above, the following method has been used, particularly when the proportion of fully saturated glyceride in the original fat is fairly large (as in mutton tallow and palm-kernel oil).

The crude oxidation product is boiled with a slight excess of sodium carbonate until a clear layer of neutral fat separates on the surface. The aqueous layer, still retaining a considerable amount of emulsified neutral fat, is syphoned off, and the separated neutral product washed by boiling with water until free from alkali. The united alkali extract and washings are now repeatedly extracted with ether as above.

By these methods a separation is ultimately achieved yielding on the one hand the acidic products of oxidation substantially free from neutral glycerides and on the other the neutral product containing only traces of acid substances. Thus in the experiment cited above, the following results were obtained:

A. White solid separated from ether and acetone—completely neutral, 12·5 g.

B. "Neutral" residue from ether, still containing a little soap, 24 g.

C. Acidic glycerides recovered from alkali solutions: partly freed from monobasic (nonoic) acids produced in the oxidation by heating at 95—100°/2 mm. until the weight became constant. Not submitted to further oxidation, 66·4 g.

B possessed an iodine number of 7·5 (original tallow, iodine number 41·2) and was reoxidised with 4 times its weight of powdered permanganate in acetone solution; the products were worked up by a combination of the methods described above, yielding 15·3 g. of neutral products (D) and 5·1 g. of acidic products (E).

Thus there were obtained in all 27·8 g. of crude neutral glyceride (A and D) and 71·5 g. of acidic glyceride (C and E).

The crude neutral glyceride (27·8 g.) was finally purified by boiling with dilute sodium carbonate solution and then repeatedly with water, the aqueous and alkaline liquors being then united as before and exhaustively extracted with ether. There was thus obtained a total proportion of 26·4% of fully saturated glycerides in the original tallow.

The fully saturated glyceride—iodine number 0·8—gave on saponification a mixture of fatty acids the mean equivalent of which was 266·5, corresponding to 59·8% of palmitic and 40·2% of stearic acid.

In another independent oxidation of mutton tallow, the fully saturated glycerides were 24·7% of the total fat—the fatty acids having a mean equivalent of 268·2.

Cacao butter. Two similar oxidations of cacao butter were undertaken with the following results:

		Expt. I.	Expt. II.	Calc.*
First oxidation	neutral product	22·1	24·7	
	iodine number	6·5	8·9	
Re-oxidation of neutral product	fully-saturated glycerides	4·8	4·8	
	iodine number	1·6	1·1	
	mean equivalent of combined fatty acids	275·4		
Combined acidic products (free from monobasic acids)		79	79·5	81·9
Mean saponification equivalent		174·0	174·4	174·7

* On the basis of 5% and 1·5% of saturated glycerides respectively.

Cotton-seed oil. The final general results obtained so far are:

	Expt. I.	Expt. II.	Calc.*
Fully saturated glycerides	1·6	1·5	
Combined acidic products (free from monobasic acids)	(80) †	68·3	73·4
Mean saponification equivalent		123·1	123·2
Combined acidic products (solids insoluble in cold ethyl acetate)	53·6		
Mean equivalent	137·6		

* On the basis of 5% and 1·5% of saturated glycerides respectively.
† Not freed from nonoic acid.

II. *Oxidation of Glycerides with Concentrated Hydrogen Peroxide and Acetic Acid.*—Neutral unsaturated fats are oxidised with much the same ease as the corresponding fatty acids or methyl esters when agitated at 40—80° with excess of concentrated hydrogen peroxide in moderately concentrated acetic acid solution. The products contain, however, not only glycerides of dihydroxystearic acid, but also a considerable proportion of the latter in the monoacetylated form. The presence of combined acetic acid in these compounds was apparent at an early stage of the investigations and, whilst at first it seemed possible that displacement of one or other higher fatty acid radical by that of acetic acid had occurred, we were able to satisfy ourselves that this took place, if at all, only to an insignificant extent, and that the quantitative data at our disposal definitely pointed to acetylation of one of the hydroxyl groups introduced.

The conditions employed in earlier work by one of us (Hilditch, J., 1926, 1828) on the oxidation of methyl oleate or oleic acid by this reagent probably led to the presence of any monoacetyl derivatives of dihydroxystearic acid or its methyl ester being overlooked, and we hope shortly to return to the study of this action in its simpler applications in the light of the present results.

In the meantime the presence of a considerable degree of acetylation in the products from hydrogen peroxide oxidation of the neutral glycerides has unfortunately complicated matters seriously, since it is obviously very difficult (although apparently not impossible) to remove the acetyl residues without at the same time hydrolysing the glycerides themselves. It is possible to reduce the amount of acetylation to some extent by conducting the process in more dilute acetic acid and at as low a temperature as possible (40—50°), but the oxidation then becomes very slow and is difficult to carry to completion even after several days. We consider at

present that the more promising procedure is to operate in concentrated acetic acid solution at a fairly high temperature; the oxidation then proceeds rapidly to completion. A description will be given of preliminary results obtained in this way with cacao butter and mutton tallow.

Cacao butter. Cacao butter (100 g.) was heated with glacial acetic acid (400 c.c.) in a wide-necked conical flask provided with a good mechanical stirrer and immersed in a water-bath maintained at 75—80°. 35% Hydrogen peroxide solution (50 c.c.) was added, further additions of 25 c.c. of this solution being made after 2 hours and after 5 hours from the commencement. After a total period of 9 hours at 75—80° with constant stirring, the product was cooled and poured into water. A large quantity of hard, tough solid separated and was removed, and the filtrate was made alkaline with excess of sodium carbonate solution and then extracted with ether several times. The solid cake was dissolved in the ethereal solution, and the whole washed with water.

The residual fat from the washed ethereal extract was boiled in water with a slight excess of dilute sodium carbonate solution, settled, and separated from the aqueous layer by siphoning off the latter, and then washed similarly and repeatedly with boiling water until neutral. The aqueous and alkaline washings were united and re-extracted with ether. There were thus obtained 101·6 g. of neutral product (95·8 g. from the aqueous extraction, and 5·8 g. recovered by ether from the aqueous layers).

All aqueous and alkaline liquors were methodically acidified and the higher fatty acids (4·3 g.) recovered.

The neutral product (101·6 g.) had an iodine number of 1·6 and a saponification equivalent of 251·5 (calc. from the known composition of the total fatty acids, 302·9 as dihydroxystearic derivative, or 225·3 if the latter are in the monoacetylated form); it contained 3·0% of combined acetic acid (as $CH_3 \cdot CO$).

From the mean equivalent (251·5) of this product, it may be calculated that (*a*) assuming displacement of fatty acid by acetic acid in the glyceride itself, the fatty acids displaced should have amounted to 22·4 g. of the total product, with production of 86·8 g. of neutral product; (*b*) assuming acetylation of the dihydroxystearic radical produced, there should have been no production of free fatty acids and a yield of 108·5 g. of neutral product.

The experimental data are thus strongly in favour of the latter hypothesis, the small amount of free fatty acid observed being accountable for by slight hydrolysis under the conditions of the reaction.

The neutral product was resolved by repeated systematic fractional crystallisation from acetone into the following fractions:

		% of whole.	Sap. eq.
A.	Least soluble; apparently homogeneous, hard, white, crystalline solid, m. p. 68—69°	22·5	293·4
B.	Sparingly soluble; hard and crystalline; gelatinises with acetone; m. p. 47°	6	256·6
C.	Intermediate fraction; soft, granular mass, m. p. 38—42° (indef.)	4	243·3
D.	From combined mother-liquors (except the first); soft, oily paste	42·5	241·1
E.	Most soluble portion from first crystallisation; oily	25	231·7

Dihydroxystearic acid (m. p. 95°) was present as glyceride in all these fractions, but a rigid method for its separate determination when mixed with palmitic and stearic acids is not yet available.

The mixed acids (mean equivalent 284·5) from fraction A, however, yielded by crystallisation from light petroleum 77% of the amount of this acid which would be required for the product derived from an original mono-oleic glyceride. This fraction apparently still contained traces of acetylated products.

Fractions D and E contained considerable quantities of acetylated products [CH_3·CO found: 3·45% (D) and 4·35% (E)].

These results indicate that the hydrogen peroxide treatment of unsaturated glycerides leads to a complicated mixture of products and that the method in its present stage of development is not adapted for quantitative work; nevertheless the above group of fractions affords confirmatory evidence of the general and to a large extent even distribution of oleic acid throughout the glycerides present in cacao butter.

Mutton tallow. Mutton tallow (100 g.) was oxidised in acetic acid with 35% hydrogen peroxide solution under exactly the same conditions as cacao butter. After 9 hours' treatment at 75—80° the mixture was cooled, and the neutral portion of the product obtained free from acetic acid and traces of fatty acid.

The neutral product (100·7 g.) had an iodine number of 1·6 and a saponification equivalent of 245·3; it contained 4·65% of acetic acid (calculated as CH_3·CO). The yield of neutral product, together with its content of combined acetic acid, points, as in the previous case, to acetylation of one of the hydroxyl groups rather than to displacement of fatty acid residues by acetic acid in the glycerides present.

The product was similar in general appearance to that from cacao butter and was separable by crystallisation from acetone into a hard, white, sparingly soluble material and more soluble constituents. Quantitative resolution of the hydroxylated tallow by

this means is at present in progress and the results will form part of a subsequent communication.

We wish to acknowledge the assistance of Mr. G. Collin (who is also engaged in the investigation of palm-kernel oil by these methods) in connexion with one of the oxidations of cotton-seed oil referred to in this paper.

THE UNIVERSITY, LIVERPOOL. [*Received, October 25th*, 1927.]

CCCCX.—*The Heat of Adsorption of Oxygen on Charcoal.*

By ANGUS FITZCHARLES HENDERSON WARD and ERIC KEIGHTLEY RIDEAL.

CALORIMETRIC determinations of the heat evolution on adsorption of oxygen by charcoal have been made by Dewar (*Proc. Roy. Soc.*, 1904, *A*, **122**, 1904), Blench and Garner (J., 1924, **125**, 1288), and Keyes and Marshall (*J. Amer. Chem. Soc.*, 1927, **49**, 156). In extending Warburg's work (*Biochem. Z.*, 1924, **145**, 461) on oxidation at charcoal surfaces, Rideal and Wright (J., 1925, **127**, 1347) and Wright (this vol., p. 2323) showed that in a sugar charcoal three different types of surface could be distinguished and their relative areas determined by the method of selective poisoning. The most active area permits autoxidation when the charcoal is shaken with water containing dissolved air or oxygen. The reaction is of zero order, due to the escape of carbon dioxide from the active patches. It is natural to suspect that the portions of the charcoal surface which, according to these observations, are readily autoxidisable would be those on which the energy change, as noted in the calorimetric experiments of Blench and Garner on adsorption of the gas, would likewise be greatest.

Since charcoal is an extremely variable material, and different results are obtained from samples prepared in different ways, it seemed desirable to use several varieties and to attempt to correlate the heats of adsorption of oxygen with other properties of the charcoal. The determination of the heats of adsorption for four different charcoals is now described, together with the rate of autoxidation, the true densities, the apparent bulk densities, the adsorption of methylene-blue at p_H 6·5, and the particle size.

EXPERIMENTAL.

The charcoals employed were: (1) Merck's blood charcoal, purified by digestion with hydrochloric acid and activated by

heating in air for ½ hour to dull redness; (2) Griffin's sugar charcoal, reignited and washed; (3) "supra-norite," made from wood dry distilled at 700° and then activated by superheated steam; (4) potash sugar charcoal, prepared by charring lump sugar with 20% of potassium carbonate in a porcelain dish and extracting the mass with hydrochloric acid, and, after prolonged reflux washing with boiling water, activated by ignition in a silver crucible. We are indebted to Dr. C. G. L. Wolf for the last three charcoals.

Determination of the Adsorption of Methylene-blue.—The adsorption isotherms of charcoal for various solutes vary greatly. With iodine or acetic acid, the amount adsorbed is proportional to the bulk concentration over a wide range; but phenol, quinine, and methylene-blue reach adsorption maxima at low concentrations (Honig, *Koll.-Chem. Beih.*, 1926, **22**, 345). Kruyt, Pincussen, and Warburg have offered various objections to the use of methylene-blue, but Paneth and Radu (*Ber.*, 1924, **57**, 1221), from experiments on powdered diamond and charcoal, conclude that the saturation maximum is attained on covering the available surface with a unimolecular layer of the dye. Methylene-blue will, however, give no indication of the extent of the micro-pores owing to the size of the molecule; for example, active coconut charcoal readily adsorbs gases and acetone, but its methylene-blue adsorption is small. The adsorption of many dyes varies with the acidity of the solution, and all determinations were conducted at p_H 6·5. A solution of methylene-blue containing 1 mg. per c.c. was added to 0·1 g. of charcoal (more in the case of sugar charcoal) from a burette until it ceased to be completely decolorised on shaking and keeping for some while. Further quantities of the dye were then added and the residual amounts in the solution were determined colorimetrically with the aid of a Klett biocolorimeter. The results, obtained on the assumptions of Paneth and Radu, that 1 mg. of dye will cover 1 sq. m. of surface, are as follows:

Charcoal.	Areas (sq. m. per g.).		Mean.
(1)	642, 644,	573, 630	622
(2)	8·4	7·5	8·0
(3)	503	546	525
(4)	6·0	5·0	5·5

The ash contents of the dried charcoals, determined by the slow ignition of about 0·5 g. and heating the residue until of constant weight, were:

Charcoal	(1)	(2)	(3)	(4)
Ash content, %	1·00	0·15	9·59	0·37

The densities of the charcoals were determined by opening specimens of charcoal sealed in glass under water after prior exhaustion with a

diffusion pump for 5 hours, the charcoals having been heated at 200° to 300° during the process of exhaustion. In such determinations there occurs a " drift " in the values obtained for the densities (Cude and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 391), due to the gradual penetration of the liquid into the micro-pores. The values obtained after 15 minutes' immersion are found to differ from the " infinity " value by about one unit in the third decimal place. This period was accordingly adopted as convenient for these experiments. The apparent bulk densities, which gave an indication of the state of aggregation, were determined by weighing the amount of the powders necessary to fill a definite volume, the tubes being tapped to ensure uniformity of packing. The values obtained were reproducible. The charcoals were also examined for possible changes in the apparent bulk densities after the experiments on the adsorption of oxygen had been completed. The results obtained are in the following tables :

		Apparent bulk density	
Charcoal.	True density.	(before).	(after).
(1)	1·37	0·22	0·22
(2)	1·42	0·58	0·58
(3)	2·03	0·14	0·115
(4)	1·43	0·30	0·32

It will be noted that charcoal (3) is relatively unstable, in that the apparent bulk density undergoes a diminution during the process of exhaustion necessary for the determination of the heat of adsorption of oxygen, although the charcoal did not lose weight to any measurable extent during evacuation. This charcoal has a true density of above 2·0, yet its bulk density is least, an indication that the ash of the charcoal probably gives a support to enable the charcoal to exist in a much more porous but unstable state.

The rates of autoxidation of the charcoals were determined at 40° with the aid of a Barcroft differential shaking machine in the manner described by Rideal and Wright (J., 1925, **127**, 1347), and are given for specimens of the charcoal both before and after the determination of the heats of adsorption of oxygen :

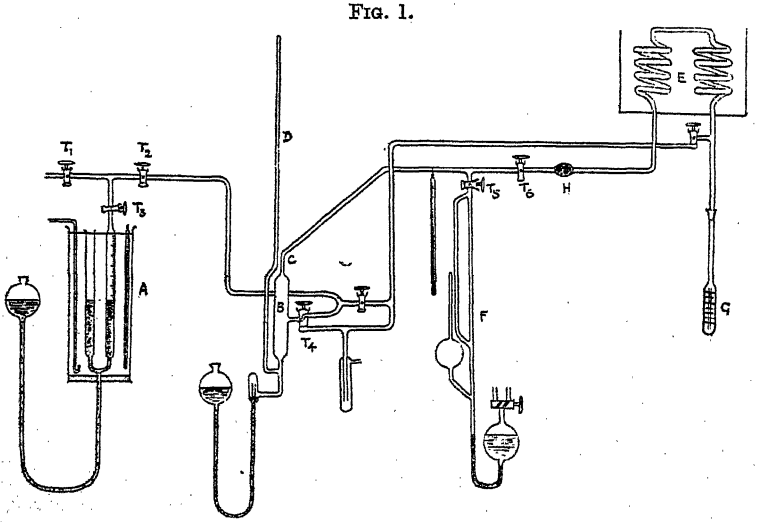
Rate of autoxidation (in mm.^{3} of O_2 at *N.T.P.* per g. per hour at 40°).

	Before adsorption experiments.			After adsorption experiments.		
Charcoal.			Mean.			Mean.
(1)	232	229	230	242	244	243
(2)	165	159	162	196	208	202
(3)	64·8	72·8	69	218	209	214
(4)	352	364	358	316	318	317

Again it will be noted that charcoal (3) is exceptional, in that the process of prolonged exhaustion necessary for the determination of the heat of adsorption has caused a very considerable increase in the autoxidisable area.

The Determination of Particle Size.—The sizes of the charcoal particles were measured with the microscope and oil-immersion objective, with a scale in the eye-piece. This was standardised by comparison with blood corpuscles (7μ diameter). Charcoals (2), (3), and (4) were fairly homogeneous, but (1) varied considerably, the largest particles being seven or eight times the smallest. For (2), (3), and (4), the maximum variation in size was 3- or 4-fold. Charcoal (1) was made up of particles of very irregular shape, charcoals (2) and (4) were almost cubic or spherical, and in charcoal (3) one-third of its particles consisted of thin rods, with a length of five or six times the thickness. The diameter given below represents for this charcoal an average value of the different dimensions. The

FIG. 1.



mean diameters of the charcoals are as follows (average of measurements on a large number of particles):

(1) 8·1μ; (2) 5·8μ; (3) 4·9μ; (4) 5·8μ.

Brownian movements were easily observed in the case of the smallest particles.

Determination of the Adsorption and Heats of Adsorption of Oxygen.—The oxygen was prepared by the electrolysis of a 10% solution of caustic soda, and passed over calcium chloride, solid potash, and phosphoric anhydride; in order to remove any hydrogen present the gas was then passed over palladium-asbestos, and again dried by phosphoric anhydride. The oxygen was introduced into the measuring burette A (Fig. 1), which was enclosed in a water jacket

kept at uniform temperature by a fine stream of air bubbles being driven through it.

In an experiment, the taps T_2 and T_3 were kept open, and a measured quantity of the gas was delivered into the vessel B by way of the three-way tap T_4. This was a hollow-barrel tap by which B could be put into communication with either the burette or the high-vacuum pumps (a Langmuir pattern mercury-vapour diffusion pump, backed by a Hyvac pump). The vacuum kept the barrel well pressed down all the time. By raising the level of the mercury in B to the mark C, the gas could be driven over *via* the tap T_6 and the spirals of capillary tubing E (kept in melting ice) into the adsorption vessel G. This was made of Pyrex glass and connected to the rest of the apparatus by a ground joint. Inside G was placed a thin rod of Pyrex with several discs on it, to keep the charcoal from being pressed down too tightly. The possible poisoning of the charcoal by mercury vapour was prevented by a small tube containing gold foil (H in the figure). The pressure of the oxygen was measured on the tube and scale D.

For the measurement of the heat of adsorption, the Bunsen ice calorimeter was used, as described by Schüller and Wartha (*Wied. Ann.*, 1877, **1**, 359). Instead, however, of their method of weighing the mercury which moved along the capillary tube, it was found sufficiently accurate, and much quicker, to measure the distance that the mercury meniscus moved along the tube by means of a scale behind. The inner tube of the calorimeter was about half filled with mercury to ensure good contact with the source of heat placed inside it. The calibration of the instrument was effected by introducing weighed amounts of various metals at known temperatures and with known specific heats, and the movement of the mercury along the scale was observed. After various methods of freezing a sheath of ice round the central tube had been tried, it was found that the most convenient method was to push down the centre an iron rod which had been cooled in liquid air. The mercury caused uniform cooling, and the ice sheath was regular.

Since the water inside the calorimeter is under a slight pressure due to the column of mercury, Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146) put a couple of drops of alcohol in the water of the surrounding vessel to depress its freezing point by the same amount and prevent the gradual movement of the mercury meniscus due to the slow melting of the ice sheath. In these experiments it was found that this effect was altogether masked by the impurity of the ice in the outer jacket, which was at a slightly lower temperature than 0°, and caused a slow freezing inside. This was decreased by first washing the ice in distilled water, but could not

be got rid of entirely; this, however, proved to be no disadvantage, for by the method adopted readings could be taken more quickly when there was a slight outward movement of the mercury.

At the beginning of an experiment, a weighed quantity of charcoal was placed in the adsorption vessel, and baked for 2 or 3 days at about 420° until the pressure decreased to about 10^{-5} mm. At the beginning of the evacuation there was always a danger of some of the charcoal being carried away owing to the rapidity of evolution of gas. To prevent this a small wad of cotton wool was placed in the tube leading out of the adsorption vessel.

When the pressure was sufficiently low, the tap T_5 was closed, and the McLeod gauge shut off from the rest of the apparatus. The ice calorimeter was then placed under the adsorption vessel and raised into position. After equilibrium had been reached (about 2 hours), a small amount of gas was transferred from the burette A into B, and then driven into the vessel C. The pressure of the oxygen, as measured on the scale D, gradually decreased as more of the gas was adsorbed, and at the end of about $\frac{1}{2}$ hour had reached its final value. More gas was then transferred from the burette, and the procedure repeated. At each reading of the pressure or volume, the temperature of the air in the neighbourhood of the apparatus and that of the water jacket round the burette were observed.

The volume of the adsorption vessel and the tubes leading to it, as far as the mark C, had previously been determined by letting in various known amounts of gas and measuring the pressure. In an actual adsorption experiment, part of the volume of the system is at room temperature, and part at 0°. The volume of the part at room temperature was found by measuring the lengths and internal diameters of the various tubes that made it up, and by subtracting this from the total volume, the volume of the part at 0° was found. The relative amounts of these two volumes need not be known so accurately as the total volume, as the error due to this is not so great.

The amount of gas adsorbed was determined as follows.

Let v_1 = volume of system at room temperature; v_2 = volume of system at 0° (allowance must be made here for the volume actually occupied by the charcoal); P = atmospheric pressure; p = pressure of gas in the system; t = room temperature; T = temperature of burette; and V = volume of gas from burette. Then if the volume of V corrected to *N.T.P.* is V',

$$V' = 273VP/760(273 + T).$$

If the volume of gas which fills v_1 becomes v_1' when reduced to *N.T.P.*, then

$$v_1' = 273v_1p/760(273 + t);$$

v_2' similarly defined would then be given by $v_2' = pv_2/760$, and the amount of gas adsorbed (in c.c. at *N.T.P.*) would be $V' - (v_1' + v_2')$. From this the amount adsorbed per g. is easily found. The results obtained with the various charcoals are given graphically, the amount of oxygen adsorbed being plotted against the pressure.

With the calorimeter in position scale readings were taken at frequent intervals and plotted against time on as large a scale as possible. In the intervals between the liberations of heat, parallel straight lines were obtained, but when the gas was let in there was a resulting inflexion in the curve, which again became straight when equilibrium was reached. The distance between the lines, measured parallel to the axis of scale readings, was proportional to the heat evolved. With the capillary tube used, the sensitivity of the instrument was about 0·5 cal. per mm. of the scale. The sensitivity of the calorimeter depends, of course, on the diameter of the capillary tube, but it is not convenient to use capillary tubes narrower than this, as the mercury sticks and makes accurate reading difficult.

By this means the evolution of heat was found for each small addition of gas, and after summing these, a curve was plotted for the total amount of heat liberated against the total amount of gas adsorbed at different pressures (integral heat of adsorption). The slope of the tangent to the curve at any point gave the differential heat of adsorption in cals. per c.c. or cals. per g.-mol. according to the scale used. These values were then plotted against the amount of gas adsorbed.

Results.

Table I is an example of the experimental results [for the charcoal (1)]. For the other charcoals similar results were obtained, but these are only shown graphically.

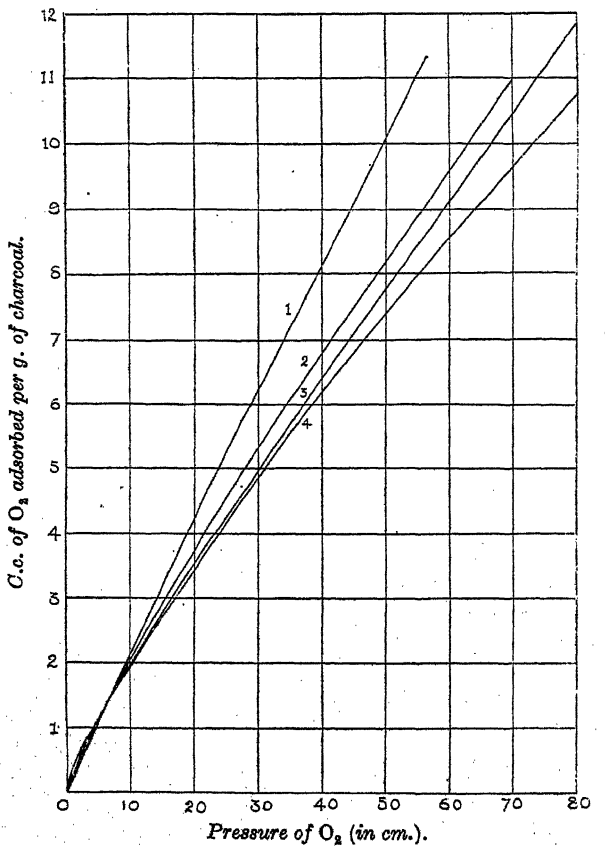
TABLE I.

Expt.	Press. of O_2 (cm.).	C.c. O_2 adsorbed per g.	Sum of differential heats (cals. per g.).	Expt.	Press. of O_2 (cm.).	C.c. O_2 adsorbed per g.	Sum of differential heats (cals. per g.).
(1) 1	11·20	2·35	0·96	(1) 3	10·85	2·38	1·20
	26·10	5·28	1·53		23·85	5·06	1·66
	40·75	8·05	2·30		35·47	7·37	2·14
(1) 2	13·20	2·90	1·62		50·80	10·37	2·64
	20·50	4·38	1·97		62·70	12·42	3·11
	38·48	8·02	2·74	(1) 4	1·52	0·28	0·48
	49·21	10·05	3·30		3·15	0·65	0·71
	71·71	14·08	4·03		8·00	1·77	1·01
(1) 3	1·00	0·21	0·38		20·53	4·54	1·39
	3·30	0·72	0·76		55·40	11·22	2·54
	5·87	1·38	0·92		70·30	13·82	3·07

The amounts of oxygen adsorbed at different pressures are shown on the adsorption isotherms (Fig. 2). For any particular

charcoal, the figures found in the different runs fall very closely on the same curve. There is not much difference in the curves for the different charcoals, (2), (3), and (4) being almost identical, and (1) slightly greater. The isotherms, although not quite straight lines, are nevertheless very far from the shape to be expected if the adsorption maximum were almost reached. They are very nearly

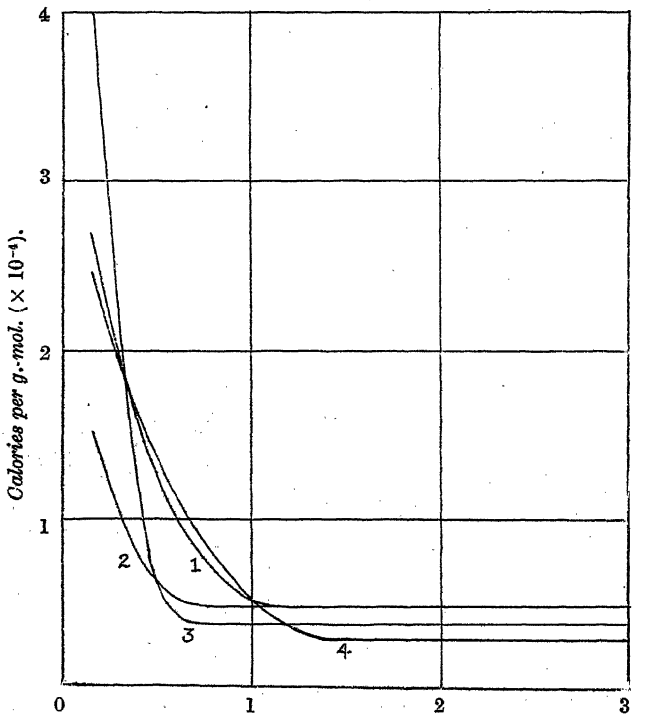
FIG. 2.



linear at the beginning of the curve, when the amount adsorbed is almost directly proportional to the pressure. Just by the origin, however, there is a slight divergence from this, especially noticeable for the charcoal (4). The curve, which is nearly straight down to about 4 cm., bends downwards and becomes slightly concave to the pressure axis; *i.e.*, at low pressures the charcoal adsorbs rather more oxygen for a given pressure increase than at higher concentrations. This effect occurs also with (2) and (3) although to a less extent.

More marked differences in behaviour between the charcoals are found when the heat of adsorption of oxygen (in cals. per g.-mol.; mean of several experiments) is plotted against the amount adsorbed, Fig. 3. For one charcoal, the agreement in this case between different runs is not nearly so good as for the adsorption isotherm. This is not due to inaccuracies of measurement, for the divergencies obtained are much greater than the possible error of the ice calori-

FIG. 3.



meter. The charcoal surface must have been altered in some way during the out-gassing between runs. As far as possible, the same temperature was used in all cases, but owing to difficulties of control, an error of 10° in the regulation was not impossible; moreover, owing to various circumstances, the out-gassing was continued for different times (1, 2, or 3 days).

The first noteworthy point about the heat evolution curves is the initial steep part, owing to the relatively high heat of adsorption for the first amount of oxygen adsorbed. On account of the small

capacity of the calorimeter system it was found impracticable to work with more than 1·5 g. of charcoal; in addition, the sensitivity was such that accurate measurements both of the amounts of oxygen adsorbed and of the corresponding thermal evolution could not be conducted on less than 0·15 c.c. adsorbed per g. With these quantities, the ascending portions of the Q,x curve noted by Garner would not be obtained, but the relatively high heats of adsorption for the initial steep portions of the curve could be accurately determined. In the graphs, the straight portions of the curve indicate uniformity of properties and a constant heat of adsorption, but the portions near the origin correspond to the areas of the charcoal more active in adsorption. From a determination of the area covered by this amount of oxygen, the area of the active patches can readily be found. The volumes of oxygen adsorbed with an increased heat evolution are approximately as follows:

Charcoal	(1)	(2)	(3)	(4)
C.c. strongly adsorbed (per g. at *N.T.P.*)	1·0	0·6	0·6	1·3

Taking the radius of the oxygen molecule as 1·81 Å. (Jeans, "Dynamical Theory of Gases"), we obtain for the respective areas

(1) 2·78 m.^{2}; (2) 1·67 m.^{2}; (3) 1·67 m.^{2}; (4) 3·62 m.^{2}.

These areas vary in the same order as do the rates of autoxidation of the charcoals. Neglecting charcoal (3), which we have noted as being extremely variable in nature and possessing a very high initial heat of adsorption for oxygen, we obtain the following ratios between the areas of the active portions and the rates of autoxidation.

(1) $2{\cdot}78/230 = 0{\cdot}0121$; (2) $1{\cdot}67/162 = 0{\cdot}0103$;
(4) $3{\cdot}62/358 = 0{\cdot}0101$.

This agreement is as satisfactory as could be expected in view of the inaccuracies in estimating the areas of the patches with high heats of adsorption. A further comparison may be made with the data on selective poisoning furnished by the experiments of Rideal and Wright (*loc. cit.*). In their experiments, it was found that poisoning of the autoxidation of a charcoal, which consumed oxygen at the rate of 0·013 mm.^{3} per mg. per hour at 40°, was effected on adsorption of $2{\cdot}38 \times 10^{15}$ molecules of amyl alcohol per mg.

With this value, and since poisoning of autoxidation appears to be a linear function of the amount adsorbed, it is possible to calculate the number of molecules of amyl alcohol which would be necessary to poison these much more active charcoals, and to compare these values, derived from entirely different charcoals and by a different method, with the quantities of oxygen adsorbed on the active areas. These data are in the following table:

Charcoal.	Rate of autoxidation (mm.^{3} per g. per hr. at 40°).	No. molecules amyl alcohol ($\times 10^{-19}$) per g. required to poison.	C.c. of O_2 adsorbed per g. with high heat of adsorption.	Equiv. no. of molecules ($\times 10^{-19}$) adsorbed per g.	Ratio, $\frac{\text{Col. 3}}{\text{Col. 5}}$.
(1)	230	4·22	1·0	2·70	1·56
(2)	162	2·96	0·6	1·62	1·83
(3)	67	1·22	0·6	1·62	0·75
(4)	358	6·56	1·3	3·52	1·86

On comparison of the data in cols. 3 and 5 for the charcoals (1), (2), and (4), it is clear that the method of poisoning with amyl alcohol and the thermal method for oxygen adsorption yield results for the extent of the autoxidisable areas of charcoals in close agreement with one another. It cannot, of course, be definitely stated that all the oxygen molecules adsorbed with a heat evolution in excess of the normal relate to the autoxidisable portion, or that the ratios in col. 6 bear any relationship to the relative covering powers of amyl alcohol and oxygen molecules on the charcoal surfaces, for there is no reason to suppose that the selectiveness of the adsorptions on the active portions of the charcoal surfaces is identical for each material. It is interesting to note that these ratios are consistent for the three stable charcoals when it is assumed that all the oxygen adsorbed with a high heat evolution is autoxidisable; if the assumption is restricted to the quantity of oxygen adsorbed with heat evolutions exceeding 10,000 (or 20,000) cals. per g.-mol., then the ratio between this quantity and the rate of autoxidation shows rapidly increasing discrepancies between the different charcoals.

Finally, Keyes and Marshall supposed that the high initial heat corresponded to the first unimolecular layer, and that the lower subsequent heats were due to the building up of thicker films of adsorbed oxygen, but as a result of our work their view seems improbable for the following reasons: The fact that the adsorption isotherm is nearly a straight line means that the charcoal is not nearly saturated; and also, to take the case of charcoal (1) which is most adsorbent, even at atmospheric pressure the oxygen only covers 1/50 of the methylene-blue area, and, on account of the large size of the molecule of the dye, this is a considerable under-estimate of the total area available for the oxygen.

Summary.

1. Experiments have been conducted on four different types of charcoal and the following properties investigated: the adsorption of oxygen and the heat of adsorption, the rate of autoxidation, the area of methylene-blue adsorption, the ash content, the true and the apparent bulk densities, and the particle size.

2. The high initial heats of adsorption have been determined and

the areas of the corresponding active patches have been found to be proportional to the rates of autoxidation of the charcoals.

3. The covering power of oxygen has been compared with that of amyl alcohol and shown to be of the same order and to have a constant ratio for all charcoals.

4. In the case of a charcoal with a high ash content, an instability of the carbon surface and a very high initial heat of adsorption for oxygen were found.

Our thanks are given to Jesus College for the provision of a Scholarship, and to the Department of Scientific and Industrial Research for a research grant to one of us (A. F. H. W.) which permitted this investigation to be carried out.

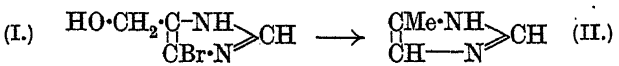
LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, November 3rd,* 1927.]

CCCCXI.—*The Condensation of Glyoxalines with Formaldehyde.*

By ROBERT GRINDLEY and FRANK LEE PYMAN.

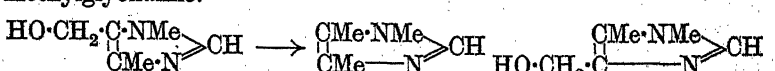
FEW examples of the condensation of glyoxalines with aldehydes have been studied hitherto. Windaus (*Ber.*, 1909, **42**, 758) has shown that the condensation product of 4(5)-methylglyoxaline and formaldehyde is 4(5)-methyl-5(4)-hydroxymethylglyoxaline, since it gave 4 : 5-dimethylglyoxaline on reduction, and Ewins (J., 1911, **99**, 2052) isolated the condensation product in a yield of 43%. Chloral also substitutes 4(5)-methylglyoxaline in the 5(4)-position (Gerngross, *Ber.*, 1912, **45**, 509), whilst both histidine (Wellisch, *Biochem. Z.*, 1913, **49**, 173) and histamine (Fränkel and Zeimer, *ibid.*, 1920, **110**, 234) yield dicyclic compounds on condensation with methylal and hydrochloric acid, the glyoxaline ring being here also substituted in the 5(4)-position. On the other hand, 5-chloro-1-methylglyoxaline condenses with formaldehyde to give 5-chloro-1-methyl-2-hydroxymethylglyoxaline in good yield (Sarasin, *Helv. Chim. Acta*, 1923, **6**, 377; 1924, **7**, 713; Sonn, Hotes, and Sieg, *Ber.*, 1924, **57**, 953, 2134) and 5-bromo-1-methylglyoxaline similarly yields a 2-hydroxymethyl derivative (Balaban and Pyman, J., 1924, **125**, 1564). Sonn, Hotes, and Sieg (*loc. cit.*) have also stated, without giving experimental details, that 1-methylglyoxaline condenses with formaldehyde mainly in the 2-position, and that 4 : 5-dibromo-1-methylglyoxaline does not condense with formaldehyde. It would thus appear from previous work that glyoxalines with a free imino-group give 4(5)-hydroxymethyl deriv-

atives, and *N*-methylated glyoxalines give 2-hydroxymethyl derivatives, whilst the accumulation of acidic groups in the molecule, as in 4 : 5-dibromo-1-methylglyoxaline, prevents condensation. The present investigation was carried out with the object of amplifying the experimental material, and the results are in harmony with the conclusions summarised above, except that it has been shown that an *N*-methylated glyoxaline may yield a 5-hydroxymethyl derivative. The ready condensation of 5-chloro-1-methylglyoxaline with formaldehyde reported by previous investigators (*supra*) was confirmed, and in our hands the yield of 5-chloro-1-methyl-2-hydroxymethylglyoxaline was 89%, but attempts to condense the isomeric 4-chloro-1-methylglyoxaline with formaldehyde under similar conditions were unsuccessful, 4-chloro-1-methylglyoxaline being recovered unchanged to the extent of 60%. As an example of an unmethylated 4(5)-halogen-substituted glyoxaline, 4(5)-bromoglyoxaline was available and this was found to give a poor yield of *4(5)-bromo-5(4)-hydroxymethylglyoxaline* (I) together with some unchanged base and much amorphous material. The constitution of the product (I) was established through its reduction by hydriodic acid and phosphorus to 4(5)-methylglyoxaline (II).



(I.) (II.)

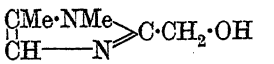
Next, the effect of the more strongly polar nitro-group was examined, and the condensation of 4(5)-nitroglyoxaline and its two isomeric *N*-methyl derivatives with formaldehyde was attempted; 4(5)-nitroglyoxaline and 4-nitro-1-methylglyoxaline were then recovered unchanged to the extent of more than 90%. 5-Nitro-1-methylglyoxaline was recovered unchanged to the extent of 68% only, this indicating that some condensation had taken place, although the presumed condensation product could not be isolated in a pure state. The condensation of the two *N*-methyl derivatives of 4(5)-methylglyoxaline was then studied. 1 : 4-Dimethylglyoxaline condensed with formaldehyde, giving a 44% yield of 1 : 4-*dimethyl*-5-*hydroxymethylglyoxaline* (III), the constitution of this product being proved through its reduction by hydriodic acid and phosphorus to the 1 : 4 : 5-trimethylglyoxaline (IV) previously made by Jowett (J., 1905, **87**, 405) by the methylation of 4 : 5-dimethylglyoxaline.



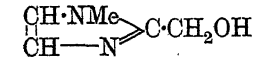
(III.) (IV.) (V.)

In earlier attempts to orient the base (III), 4(5)-methyl-5(4)-hydroxymethylglyoxaline was methylated, a mixture of (III)

with the isomeric 1 : 5-dimethyl-4-hydroxymethylglyoxaline (V) being expected. The only methylation product isolated in a pure state was not identical, but isomeric, with (III) and is consequently 1 : 5-*dimethyl*-4-*hydroxymethylglyoxaline* (V). The condensation of 1 : 5-dimethylglyoxaline with formaldehyde, however, did not give rise to this product but to an isomeride, which must consequently be 1 : 5-*dimethyl*-2-*hydroxymethylglyoxaline* (VI). Its constitution was confirmed by reduction, a trimethylglyoxaline being thus obtained which was not identical with 1 : 4 : 5-trimethylglyoxaline, and must consequently be 1 : 2 : 5-*trimethylglyoxaline* (VII).

(VI.)  (VII.)

The condensation of 1-methylglyoxaline with formaldehyde gave 1-*methyl*-2-*hydroxymethylglyoxaline* (VIII) as stated by Sonn, Hotes, and Sieg (*loc. cit.*), the yield being more than 60%. The constitution of this base was established through its reduction to 1 : 2-dimethylglyoxaline (IX).

(VIII.)  (IX.)

Finally, the condensation of glyoxaline with formaldehyde was studied, but no crystalline products could be isolated.

EXPERIMENTAL.

Condensation of Glyoxalines with Formaldehyde.—The general method of procedure was as follows: The glyoxaline base and 40% aqueous formaldehyde (abbreviated below to formaldehyde) were enclosed in a sealed tube or pressure bottle and heated in an oil-bath. Except in the cases of 4(5)-nitroglyoxaline and 4-nitro-1-methylglyoxaline, the products were worked up by adding picric acid (1 mol.) in hot aqueous solution; as a rule, resinous picrates then separated first, followed by the crystalline picrates of the hydroxymethyl compound and of the unchanged glyoxaline in this order. The identity of the material recovered unchanged was established in each case by the mixed m. p. method.

4(5)-*Nitroglyoxaline and Formaldehyde.*—(*a*) 4(5)-Nitroglyoxaline (7·0 g.) and formaldehyde (10 c.c.; 2·3 mols.) were heated for 3 hours at 125°. The base was then mainly undissolved, and after washing with water and crystallisation from glacial acetic acid, 6·83 g. of unchanged 4(5)-nitroglyoxaline, m. p. 311—312° (corr.), were recovered; yield, 97·6%.

(*b*) 4(5)-Nitroglyoxaline (2·0 g.) and formaldehyde (2·8 c.c.; 2·2 mols.), heated for 6 hours at 150°, gave 1·92 g. of recovered 4(5)-nitroglyoxaline, m. p. 310—312° (corr.); yield, 96·0%.

4-Nitro-1-methylglyoxaline and Formaldehyde.—4-Nitro-1-methylglyoxaline (1·08 g.) and formaldehyde (1·9 c.c.; 3 mols.) were heated for 5 hours at 135°. The base was then mainly undissolved, and after crystallisation from water 0·98 g. of unchanged 4-nitro-1-methylglyoxaline, m. p. 134° (corr.), was recovered; yield, 90·8%.

5-Nitro-1-methylglyoxaline and Formaldehyde.—(*a*) 5-Nitro-1-methylglyoxaline (0·65 g.) and formaldehyde (1·6 c.c.; 4 mols.) were heated for 5 hours at 125°. The product gave with hot aqueous picric acid, first resinous picrates, then crude 5-nitro-1-methylglyoxaline picrate. This was recrystallised from water, 0·64 g., m. p. 151—152°, and 0·60 g., m. p. 149—151°, being obtained; yield, 68·1%.

(*b*) A similar result was obtained on heating the reactants for 6 hours at 130°, 5-nitro-1-methylglyoxaline picrate being recovered in 52% yield together with a resinous picrate. In both cases, the base and hydrochloride prepared from the resinous picrate failed to crystallise.

4(5)-Bromoglyoxaline and Formaldehyde.—This condensation was carried out under various conditions as shown below, and the products were worked up as picrates. The fourth column gives the yield (*a*) of 4(5)-bromo-5(4)-hydroxymethylglyoxaline isolated as pure picrate, and the fifth the yield (*b*) of 4(5)-bromoglyoxaline recovered as pure picrate. Considerable quantities of resinous picrates were also obtained.

Mols. CH_2O used.	Duration of heating (hrs.).	Temp.	*a*, %.	*b*, %.
2·5	2	110°	Nil	98·1
3	1	150	,,	53·7
1·5	2	150	,,	42·7
3	3	150	8·8	30·0
3	4	150	9·3	35·2
3	5	150	10·4	10·6
3	8	150	0·3	Nil
3	3½	160	1·5	3·8

4(5)-Bromo-5(4)-hydroxymethylglyoxaline (I) crystallises from alcohol in colourless plates, m. p. 116—117° (corr.), which contain $\frac{1}{2}H_2O$ (Found, in air-dried base: loss at 80°, 5·3. $C_4H_5ON_2Br,\frac{1}{2}H_2O$ requires H_2O, 4·8%. Found in dried base: C, 26·9; H, 3·0. $C_4H_5ON_2Br$ requires C, 27·1; H, 2·8%). It is sparingly soluble in cold water, readily soluble in alcohol, acetone, or chloroform, but insoluble in ether or benzene. The *hydrochloride* crystallises from alcohol in colourless prisms, m. p. 157° (corr.; eff.) [Found in salt dried at 100° (loss 0·8%): C, 22·5; H, 2·8. $C_4H_5ON_2Br,HCl$ requires C, 22·5; H, 2·8%]. It is very easily soluble in water, and easily soluble in hot alcohol or concentrated hydrochloric acid.

The *picrate* crystallises from water in yellow, lustrous, serrated

needles, containing $1H_2O$, which is lost at 95° but not in a vacuum over sulphuric acid at the ordinary temperature. The dried salt has m. p. 180° (corr.). It is sparingly soluble in cold water, but readily soluble in hot water, alcohol, or acetone (Found in air-dried salt: loss at 95°, 4·5. $C_4H_5ON_2Br,C_6H_3O_7N_3,H_2O$ requires H_2O, 4·3%. Found in dried salt: C, 29·3; H, 2·2. $C_4H_5ON_2Br,C_6H_3O_7N_3$ requires C, 29·6; H, 2·0%).

Reduction. 4(5)-Bromo-5(4)-hydroxymethylglyoxaline hydrochloride (0·45 g.), hydriodic acid (1·9 c.c.; *d* 1·7), and red phosphorus (0·13 g.) were heated in a sealed tube for 5½ hours at 160°. The product was diluted with water, filtered, and extracted with chloroform whilst acid to remove impurities. The aqueous solution was then concentrated, saturated with potassium carbonate, and extracted first with chloroform, then with ether. The extracts were converted into picrates, and gave 0·55 g. of 4(5)-methylglyoxaline picrate, m. p. 159—160° (corr.), alone or mixed with a known specimen; yield, 83·9%.

4-*Chloro*-1-*methylglyoxaline and Formaldehyde.*—4-Chloro-1-methylglyoxaline (1·77 g.) and formaldehyde (5·5 c.c.; 4·8 mols.) were heated for 4 hours at 130°, and the product was converted into picrates; 3·16 g. of 4-chloro-1-methylglyoxaline picrate, m. p. 166°, were obtained (yield, 60·2%) together with a resinous picrate. The base and hydrochloride from the latter failed to crystallise.

5-*Chloro*-1-*methylglyoxaline and Formaldehyde.*—5-Chloro-1-methylglyoxaline (1·08 g.) and formaldehyde (2·4 c.c.; 3·5 mols.), heated for 8 hours at 135—140°, gave 5-chloro-1-methyl-2-hydroxymethylglyoxaline, isolated as picrate, m. p. 151° (corr.), in 89% yield. Sarasin (*loc. cit.*) and Sonn, Hotes, and Sieg (*loc. cit.*) record yields of 95 and 80% respectively.

1 : 4-*Dimethylglyoxaline and Formaldehyde.*—1 : 4-Dimethylglyoxaline (10·6 g.) and formaldehyde (22·3 c.c.; 3 mols.) were heated for 6 hours at 125°, and the product was converted into picrates and crystallised fractionally from water and methyl alcohol; 17·5 g. of pure 1 : 4-dimethyl-5-hydroxymethylglyoxaline picrate (yield, 44·6%) were obtained together with 1·43 g. of pure 1 : 4-dimethylglyoxaline picrate (yield, 4·0%).

1 : 4-*Dimethyl*-5-*hydroxymethylglyoxaline* (III) crystallises from absolute alcohol in small, colourless prisms, m. p. 126—127° (corr.) (Found: C, 57·0; H, 8·0; N, 22·0. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9; N, 22·2%). It is very readily soluble in water or alcohol, readily soluble in chloroform, but very sparingly soluble in ether.

The *hydrochloride* crystallises from concentrated hydrochloric acid in colourless plates, m. p. 145° (corr.), which are very hygroscopic.

The *hydrogen oxalate* crystallises from absolute alcohol in colourless prisms, m. p. 106—107° (corr.) (Found: C, 44·6; H, 5·6. $C_6H_{10}ON_2,C_2H_2O_4$ requires C, 44·4; H, 5·6%). It is very readily soluble in water, less soluble in cold alcohol.

The *picrate* crystallises from water in yellow prisms, m. p. 167—168° (corr.), which suffer no loss at 110°. It is sparingly soluble in cold water, alcohol, or acetone, but readily soluble in the hot solvents. Attempts to estimate carbon and hydrogen in this salt were frustrated by explosions.

Reduction. 1 : 4-Dimethyl-5-hydroxymethylglyoxaline (0·63 g.), hydriodic acid (1·5 c.c.; *d* 1·7), and red phosphorus (0·082 g.) were heated in a sealed tube for 6 hours at 160°. The product was diluted with water, filtered, made strongly alkaline with sodium hydroxide, and extracted with chloroform and ether. The extracts were converted into picrates and gave 1 : 4 : 5-trimethylglyoxaline picrate in 79% yield (1·26 g., m. p. 218—219°, + 0·08 g., m. p. 215—216°). This salt was identified by the mixed m. p. method, with the help of a specimen of 1 : 4 : 5-trimethylglyoxaline picrate, m. p. 218°, prepared by Jowett (J., 1905, **87**, 405) for which we are indebted to the Wellcome Chemical Research Laboratories. The salt was also analysed (Found: C, 42·7; H, 3·9. Calc.: C, 42·9; H, 3·8%), and from it the base was prepared. This was not completely purified (it had m. p. 39—40°; Jowett gives 46°), but was converted into the chloroaurate. This had m. p. 201° (corr.) (Jowett gives 202°) (Found: Au, 43·6. Calc.: Au, 43·8%).

1 : 5-*Dimethylglyoxaline and Formaldehyde.*—1 : 5-Dimethylglyoxaline (1·4 g.) and formaldehyde (4·9 c.c.; 4·5 mols.) were heated for 6 hours at 130° and the product was converted into picrates, 1·75 g. of pure 1 : 5-dimethyl-2-hydroxymethylglyoxaline picrate (yield, 33·8%) and 2·06 g. of 1 : 5-dimethylglyoxaline picrate, m. p. 163—164° (yield, 43·5%), being isolated. Under milder conditions (4 hours at 115—120°) no condensation product was isolated, but 1 : 5-dimethylglyoxaline was recovered as picrate in 83% yield.

1 : 5-*Dimethyl-2-hydroxymethylglyoxaline* (VI) crystallises from absolute methyl alcohol in colourless, hexagonal plates, m. p. 126—127° (corr.) (Found in air-dried base: loss at 110°, 4·1. $C_6H_{10}ON_2,\frac{1}{2}H_2O$ requires H_2O, 6·7%. Found in dried base: C, 57·4; H, 7·9. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9%). It is very readily soluble in water, readily soluble in methyl or ethyl alcohol or chloroform, but very sparingly soluble in ether. A mixture of approximately equal parts of this base and 1 : 4-dimethyl-5-hydroxymethylglyoxaline, which also melts at 126—127°, had m. p. 76—80°.

The *picrate* crystallises from water in small, yellow, anhydrous prisms, m. p. 174° (corr.) (Found: C, 40·7; H, 3·9; N, 19·6. $C_6H_{10}ON_2,C_6H_3O_7N_3$ requires C, 40·6; H, 3·7; N, 19·7%). It is sparingly soluble in cold water or alcohol.

Reduction. 1 : 5-Dimethyl-2-hydroxymethylglyoxaline (0·39 g.), hydriodic acid (0·9 c.c.; *d* 1·7), and red phosphorus (0·051 g.) were heated in a sealed tube for 6 hours at 160°. After dilution, filtration, and extraction with chloroform to remove impurities, the liquor was saturated with potassium carbonate and extracted with chloroform, which took up a brown mobile oil (0·37 g.) having a faint pyridine-like odour. This was converted into picrate; 1 : 2 : 5-trimethylglyoxaline picrate (0·97 g.; m. p. 204°; yield 92·2%) was then obtained.

1 : 2 : 5-*Trimethylglyoxaline picrate* (VII) crystallises from water in long, pale yellow, lustrous, anhydrous needles, m. p. 208—209° (corr.) (Found: C, 42·6; H, 4·0; N, 20·7. $C_6H_{10}N_2,C_6H_3O_7N_3$ requires C, 42·5; H, 3·8; N, 20·6%). It is sparingly soluble in cold water or alcohol. A mixture of approximately equal parts of this salt with 1 : 4 : 5-trimethylglyoxaline picrate (m. p. 218°) had m. p. 194—195°. The base prepared from the pure picrate did not crystallise, and was converted into the *chloroaurate*, which crystallised from dilute hydrochloric acid in orange-yellow, anhydrous plates, m. p. 186—187° (corr.) (Found: Au, 43·6. $C_6H_{10}N_2,HAuCl_4$ requires Au, 43·8%).

Methylation of 4(5)-*Methyl*-5(4)-*hydroxymethylglyoxaline.*—Attempts to methylate this base by heating with either methyl iodide or methyl sulphate failed, for no crystalline substance other than a small proportion of the unchanged material could be isolated (as picrate) from the reaction product, but methylation with methyl sulphate and aqueous sodium hydroxide was more successful.

4(5)-Methyl-5(4)-hydroxymethylglyoxaline (2·35 g.) was methylated by the gradual addition with shaking of 10% aqueous sodium hydroxide (23·6 c.c.) and methyl sulphate (2·4 c.c.). After the mixture had been kept for 2 hours, chloroform extracted a yellowish-brown, crystalline mass (0·8 g.), which was converted into picrate and this crystallised from water, 0·5 g. of pure 1 : 5-dimethyl-4-hydroxymethylglyoxaline picrate being obtained: yield, 6·7%.

1 : 5-*Dimethyl*-4-*hydroxymethylglyoxaline* (V) crystallises from absolute methyl alcohol in colourless, hexagonal plates, m. p. 164—165° (corr.) (Found: C, 57·2; H, 8·0. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9%). It is very readily soluble in water, and readily soluble in methyl or ethyl alcohol, acetone, or chloroform. The *picrate* crystallises from water in small, pale yellow, anhydrous prisms, m. p. 178—179° (corr.) (Found: C, 40·7; H, 3·7; N, 19·5.

$C_6H_{10}ON_2,C_6H_3O_7N_3$ requires C, 40·6; H, 3·7; N, 19·7%). It is sparingly soluble in cold water or alcohol.

1-*Methylglyoxaline and Formaldehyde.*—(*a*) 1-Methylglyoxaline (2·8 g.) and formaldehyde (4·6 c.c.; 3·5 mols.) were heated for 5 hours at 140°. The product was converted into picrates, and these crystallised fractionally from water. First, a molecular compound of 1-methyl-2-hydroxymethylglyoxaline picrate and 1-methylglyoxaline picrate (5·48 g.; m. p. 144—145°) separated, then 1-methyl-2-hydroxymethylglyoxaline picrate (4·42 g.; m. p. 137°). The yield of 1-methyl-2-hydroxymethylglyoxaline is thus 62·6%, whilst 24·6% of 1-methylglyoxaline was recovered unchanged. (*b*) 1-Methylglyoxaline (3·1 g.) and formaldehyde (4·4 c.c.; 3·0 mols.), heated for 4 hours at 130°, gave 11·35 g. of the picrate, m. p. 144—145°, and some 1-methylglyoxaline picrate (0·11 g.; m. p. 158°). The yield of 1-methyl-2-hydroxymethylglyoxaline is here 46·1%, whilst 47·0% of 1-methylglyoxaline was recovered unchanged.

1-*Methyl-2-hydroxymethylglyoxaline* (VIII) crystallises from chloroform in colourless prisms, m. p. 116° (corr.) [Found in base dried at 80° (loss 1·3%): C, 53·4; H, 7·0. $C_5H_8ON_2$ requires C, 53·6; H, 7·1%]. It is readily soluble in water or alcohol, soluble in hot acetone or chloroform, but insoluble in ether or benzene. It is not volatile in steam. The picrate crystallises from water in small, yellow, lustrous prisms, m. p. 138° (corr.) [Sonn, Hotes, and Sieg (*loc. cit.*) give m. p. 136—137° (uncorr.)] (Found: loss at 100°, 3·3. $C_5H_8ON_2,C_6H_3O_7N_3,\frac{1}{2}H_2O$ requires H_2O, 2·6%. Found in dried salt: C, 38·8; H, 3·2. $C_5H_8ON_2,C_6H_3O_7N_3$ requires C, 38·7; H, 3·2%). It is very sparingly soluble in cold water.

Reduction. 1-Methyl-2-hydroxymethylglyoxaline (0·7 g.), hydriodic acid (1·4 c.c.; *d* 1·7), and red phosphorus (0·06 g.) were heated at 155—160° for 5 hours, and the product was worked up in the usual way; 1:2-dimethylglyoxaline picrate (0·6 g.; yield 29·5%; m. p. 178—179°, alone or mixed with an authentic specimen for which we are indebted to the Wellcome Chemical Research Laboratories) was then obtained together with 1-methyl-2-hydroxymethylglyoxaline picrate (0·49 g.; yield 23·0%; m. p. 136—137°).

The *molecular compound* of 1-methyl-2-hydroxymethylglyoxaline picrate and 1-methylglyoxaline picrate crystallises from water in pale yellow needles, m. p. 145—146° (corr.) [Found in air-dried salt: loss at 100°, 1·1. $C_4H_6N_2,C_5H_8ON_2,(C_6H_3O_7N_3)_2,\frac{1}{2}H_2O$ requires H_2O, 1·4%. Found in dried salt: C, 38·8; H, 3·2; N, 21·7. $C_4H_6N_2,C_5H_8ON_2,(C_6H_3O_7N_3)_2$ requires C, 38·7; H, 3·1; N, 21·5%]. It is almost insoluble in cold water, but readily soluble in hot water. A mixture of this picrate with 1-methyl-2-hydroxy-

methylglyoxaline picrate (m. p. 138°) melted at 129—130°, whilst a mixture with 1-methylglyoxaline picrate (m. p. 159°) melted at 139—140°. On converting the picrate, m. p. 145—146°, into the corresponding bases and distilling with steam, 1-methylglyoxaline was carried over and 1-methyl-2-hydroxymethylglyoxaline remained unvolatilised. The separated bases were then converted into picrates and identified in the usual way. The constitution of the picrate, m. p. 145—146°, as an equimolecular compound of the picrates of 1-methyl-2-hydroxymethylglyoxaline and 1-methylglyoxaline was confirmed by preparing it from the two salts.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, November 9th*, 1927.]

CCCCXII.—*The Oxide-ring Structure of Normal and γ-Derivatives of Mannose. Preparation and Oxidation of Derivatives of γ-Mannonolactone and δ-Mannonolactone, with an Addendum on the Formulation of Normal and γ-Sugars as Derivatives of Pyran and Furan and the Suggestion of a New Nomenclature.*

By EDWARD HAGUE GOODYEAR and WALTER NORMAN HAWORTH.

IN continuing the study of lactones derived from sugars we have prepared several new derivatives in the mannose series. The ordinary γ-mannonolactone (III) was first prepared from mannonic acid by Fischer and Hirschberger (*Ber.*, 1889, **22**, 3218) and was obtained in purer condition by Nef (*Annalen*, 1914, **403**, 306) and by Hedenburg (*J. Amer. Chem. Soc.*, 1915, **37**, 345). The latter two authors also isolated an isomeric lactone, described originally as the "β" lactone, which is also obtainable from mannonic acid by adopting a different procedure for the anhydridation. We recommend that this "β" lactone should now be regarded as the δ-mannonolactone (VI) in view of the results obtained in a comparative study of lactones (compare Haworth and Nicholson, J., 1926, 1899). In the case of the parallel example from gluconic acid, the supposed "β" gluconolactone also should be described as δ-gluconolactone.

By solution of γ-mannonolactone in dry acetone containing 0·1% of hydrogen chloride, we have prepared the crystalline *γ-mannonolactone-monoacetone*, and under slightly different conditions the crystalline γ-mannonolactone-diacetone (II) has also been obtained. The latter is identical with the substance originally prepared by

Ohle and Berend (*Ber.*, 1925, **58**, 2590) from mannose-diacetone (I) by oxidation to the diacetone of mannonic acid, which, by loss of water, passes into the corresponding lactone. Specimens have been prepared by each of these methods and their identity established. The constitution (I) assigned to mannose-diacetone therefore receives confirmation.

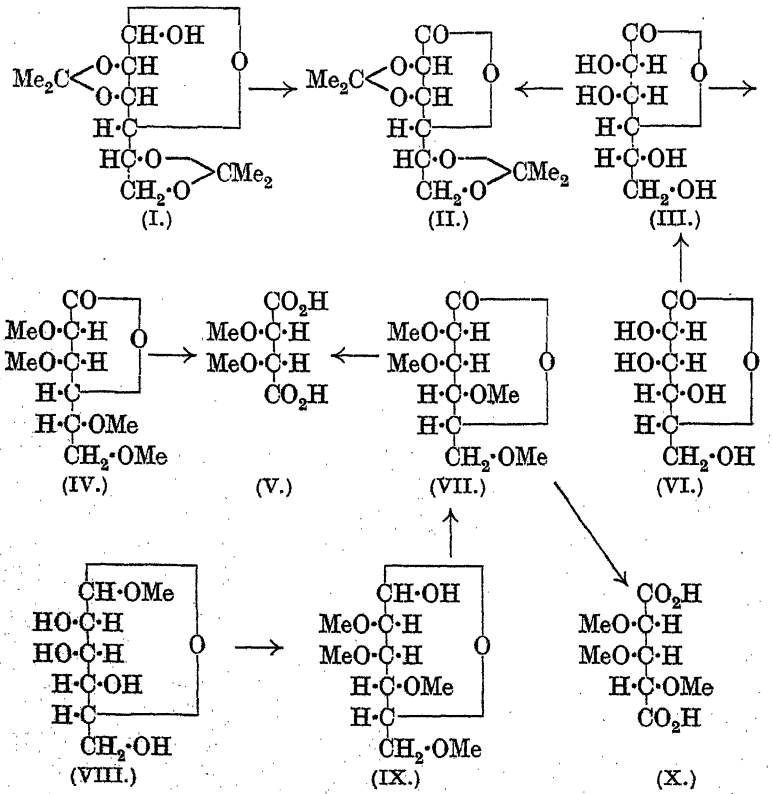
By methylation of γ-mannonolactone-monoacetone the crystalline *dimethyl γ-mannonolactone-monoacetone* was isolated, and on hydrolysis with dilute mineral acid this gave *dimethyl mannonolactone*. Acetylation of γ-mannonolactone gave rise to the *tetra-acetyl* derivative.

When γ-mannonolactone was methylated with methyl iodide and silver oxide in the presence of acetone, that is, under the conditions described by Levene and Simms (*J. Biol. Chem.*, 1925, **65**, 46), a mixture of crystalline products was obtained, from which were isolated (*a*) tetramethyl γ-mannonolactone (IV), which gave a crystalline *phenylhydrazide*, and (*b*) dimethyl γ-mannonolactone-monoacetone, identical with the specimen above-mentioned. When, however, acetone was avoided as a solvent during the methylation of γ-mannonolactone, only tetramethyl γ-mannonolactone was obtained. This showed $[\alpha]_D^{18°}$ + 65·2° falling to 61·2° in 9 days (compare Drew, Goodyear, and Haworth, this vol., pp. 1242—3).

In an attempt to prepare the tetramethyl derivative from δ-mannonolactone by direct methylation, we were only able to recognise in the products the tetramethyl γ-mannonolactone, and it seems clear that the 1 : 5 ring in the unsubstituted δ-lactone undergoes conversion into a 1 : 4 ring under the conditions employed. During the process of methylation, water is formed; this appears to open the lactone ring, which again closes to give the stable γ-lactone. The tetramethyl δ-mannonolactone was prepared, however, from α-methylmannoside (VIII) by the indirect method, namely, methylation followed by hydrolysis to normal tetramethyl mannose (IX) and oxidation of this sugar by means of bromine water. The tetramethyl δ-mannonolactone (VII) is isolated by conversion first into the crystalline phenylhydrazide, and after regeneration from this derivative is recognisable as a crystalline product, m. p. 23—25°, having $[\alpha]_D^{18°}$ + 150° (initial).

The constitution of each of these tetramethyl derivatives was determined by direct oxidation with nitric acid. Tetramethyl γ-mannonolactone (IV) gave on oxidation *i*-dimethoxysuccinic acid (V), which was identified as the crystalline methyl ester and as the crystalline *methylamide*, the latter being compared with a specimen prepared from *meso*tartaric acid by Haworth and Jones (this vol.,

p. 2352). This lactone should therefore be indexed as 2 : 3 : 5 : 6-tetramethyl mannonolactone (IV). The corresponding δ-lactone (VII) gave on oxidation a small yield of *i*-dimethoxysuccinic acid (V) and also, in a larger yield, *d*-arabo-trimethoxyglutaric acid (X), which was identified as the crystalline methylamide (m. p. 209)°. This was enantiomorphous with a specimen of the methylamide of the *l*-variety of the acid obtained by Haworth and Jones (*loc. cit.*), with which it was compared. This δ-lactone should therefore be indexed as 2 : 3 : 4 : 6-tetramethyl mannonolactone (VII).



The bearing of these results on the structure of the constituent sugars is evident. Since a lactone of formula (VII) is derived from tetramethyl mannose (IX), which in turn has been prepared from α-methylmannoside, it follows that the latter has a 1 : 5 or amylene oxide ring structure (VIII). Similarly it has been shown that mannose-diacetone is a derivative of γ-mannose (I) (Irvine and Skinner, J., 1926, 1089; compare Ohle and Berend, *loc. cit.*). This

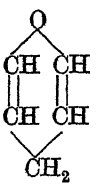
gives rise on oxidation to the same γ-mannonolactone-diacetone (II) as we have obtained direct from γ-mannonolactone (III), and since the latter gives on methylation a tetramethyl γ-mannonolactone of constitution (IV), it is demonstrated that the γ-mannose derivative has a constitution containing a butylene or 1 : 4 oxide ring. This conclusion is, however, dependent upon there having been no displacement of the ring during methylation of the γ-lactone, and this is unlikely to have occurred; and secondly upon there having been no such displacement during the introduction of acetone residues into the γ-mannonolactone. The latter contingency also is on the whole unlikely, because the γ-lactone contains two pairs of hydroxyl groups which are already favourably situated for *cis*-condensation with acetone residues and are also attached to contiguous carbon atoms. Moreover the γ-lactone is the stabilised form into which the δ-lactone is convertible.

The results now communicated assign to the mannose derivatives of the normal and the γ-series the same structural relationships as those of the normal and the γ-derivatives of glucose, of fructose, of arabinose, and of xylose, all of which have been shown by direct oxidation methods applied to their related lactones to be amylene oxides in their normal forms and butylene oxides in their labile or γ-forms (Avery, Haworth, and Hirst, this vol., p. 2308; Haworth, Hirst, and Learner, *ibid.*, p. 2432; Haworth, Hirst, and Miller, *ibid.*, p. 2436; Haworth and Jones, *loc. cit.*). In a later paper it will be shown that these same structural relationships have been fully proved also for galactose in its normal and γ-forms. So far, therefore, as it is possible to generalise from these direct oxidation results it is seen that the conclusions reached confirm entirely the structural formulæ which were adduced from a study of the comparative rates of hydrolysis of the two series of lactones in aqueous solution, as determined (*a*) by the polarimetric method (Drew, Goodyear, and Haworth, *loc. cit.*) and (*b*) by the conductivity method. The generalisation advanced by Charlton, Haworth, and Peat (J., 1926, 89), which stated that the normal sugars tend to exist in amylene oxide forms and the labile or γ-sugars in butylene oxide forms, is again supported by the collateral data obtained from the oxidation of the methylated lactones.

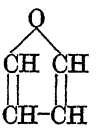
Addendum.

The normal sugars are thus seen to be representatives of the parent form indicated by pyran, and the labile or γ-sugars have as their parent substance furan. The two types of normal and labile sugars might well be described as the pyran- and furan-types. Thus, arabinose in its normal form is tetrahydroxytetrahydropyran

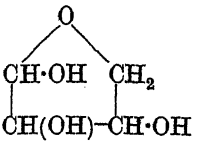
(A), whilst in its labile or γ-form it is tetrahydroxymethyltetrahydrofuran (B).



Pyran.

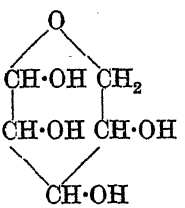


Furan.

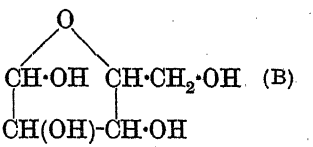


Furanose (a tetrose)
(Trihydroxytetrahydrofuran).

(A)



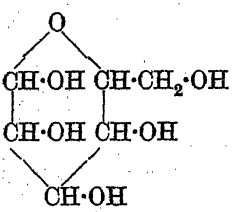
A Normal Pentose.
[Pyranose (Arabo-, etc.)].



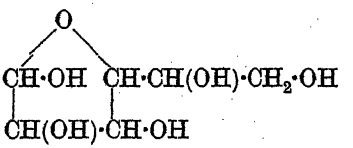
(B)

A γ-Pentose.
[Xylo-furanose (and also Arabo-, ribo-, lyxo-furanose)].

(C)



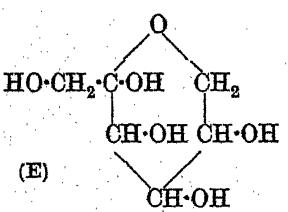
A Normal Aldo-hexose
[Gluco (etc.) -pyranose].



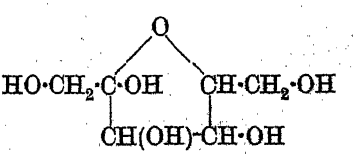
(D)

A γ-Aldo-hexose.
[Gluco (etc.) -furanose].

(E)



A Normal Keto-hexose.
[Fructo-pyranose].



(F)

A γ-Keto-hexose.
[Fructo-furanose].

There is urgent need for the adoption of a simplified, concise, standard nomenclature in the sugar group which will define the essential structural differences between a normal sugar form and a labile or so-called γ-sugar form. Such a revised nomenclature should be capable of expressing also the stereochemical relationships

of the various pentoses, hexoses, etc., which may occur in either structural form.

On the basis of the conclusions now reached, the formula (A) must be accepted as a general representation of a normal sugar, which might be described as a pyranose. The normal sugars arabinose, xylose, etc., may then be described as arabo-*pyran*ose, xylo-*pyran*ose, and both the structure and the configuration would be at once intelligible from this nomenclature. The corresponding labile or γ-isomerides may be described as arabo-*furan*ose, xylo-*furan*ose, etc. (B). Proceeding in a similar manner to the representation of a hexose, it is only necessary to modify the formula (A) by the introduction of a primary alcohol group as a side chain, in order to indicate (as a hexa-pyranose) the structural relationships of the normal hexoses, and this modification, having regard to both the structural and the stereochemical arrangement involved, would be recognisable under the name of gluco-*pyran*ose (C), manno-*pyran*ose, galacto-*pyran*ose, etc., whilst the labile or γ-sugars would similarly be described as gluco-*furan*ose, manno-*furan*ose, etc. (D).

Similarly in the cases of normal and γ-fructoses, which have been shown by one of us to have the constitutional formulæ (E) and (F), the corresponding nomenclature would apply: fructo-*pyran*ose for the normal sugar, and fructo-*furan*ose for the labile form (Haworth and Hirst, J., 1926, 1858; Haworth, Hirst, and Learner, this vol., p. 1040; Haworth, Hirst, and Nicholson, *ibid.*, p. 1513; Avery, Haworth, and Hirst, *loc. cit.*; Haworth, Hirst, and Learner, this vol., p. 2432).

The sugars higher in the series, such as the heptoses, occurring in either form would be definable as hepta-*pyran*oses or hepta-*furan*oses, the device which is already current being used for distinguishing between the configurations, namely, glucohepta-*pyran*ose, etc., instead of "glucoheptose (normal) of the amylene oxide form."

It is not without significance that the naturally occurring pigments such as the anthocyanins, occurring as glucosides, contain as an essential part of their structure a pyran residue, and that the anthoxanthins or hydroxyflavones contain the related pyrone group. It is conceivable that this residue is traceable to its origin as a normal sugar, suggesting that these colouring matters of plants are transformation products intimately related in their structure to the sugar group. The suggestion has already been made that phenols originate through an aldol type of condensation between the aldehyde group of an aldohexose of position (6) in the chain, giving a hexahydroxyhexahydrobenzene of the type of inositol, which then passes by elimination of water to the polyhydric phenols (Haworth, *J. Soc. Chem. Ind.*, 1927, **46**, 295). On the other

hand, the frequent occurrence of furan residues in natural products suggests that these are similarly traceable to the pre-existing γ-sugar. We have already shown that tetramethyl γ-fructose passes with remarkable ease into a furan derivative (Haworth, Hirst, and Nicholson, this vol., p. 1513).

EXPERIMENTAL.

Methylation of γ-Mannonolactone.—Crystalline γ-mannonolactone, prepared by the methods described by Nef and by Hedenburg (*loc. cit.*), was methylated with methyl iodide and silver oxide in presence of methyl alcohol as solvent. The product was treated with the same reagents in the presence of acetone (Levene and Simms, *J. Biol. Chem.*, 1925, **65**, 46) and thereafter twice with the methylating agents without any extraneous solvent; it then became partly crystalline. This product was distilled under diminished pressure, subjected to two further methylations, and again distilled. The major portion (70% yield), b. p. 100—105°/0·06 mm., became partly crystalline and the crystals were collected on porous tile and recrystallised from light petroleum (voluminous needles, m. p. 109—110°). A second crop consisted of both needles and plates, m. p. 83°. Recrystallisation of the latter from boiling carbon tetrachloride gave prisms, m. p. 110°, showing no depression of melting point in admixture with the needles. This material gave OMe, 30·25%. It was clear that the compound crystallising in needles could also be obtained from carbon tetrachloride in the form of prisms. It showed $[\alpha]_D^{20°}$ + 64·2° in water ($c = 1·1$), changing to + 55·8° in 9 days (Found: C, 53·5; H, 7·3. $C_{11}H_{18}O_6$ requires C, 53·6; H, 7·3%). These analytical figures agree with those required for a *monoacetone* derivative of dimethyl γ-mannonolactone, and that this was actually the product obtained was shown by an alternative method of preparation which is described later.

In order to investigate the reason for the occurrence of this compound a further lot of γ-mannonolactone was methylated (*a*) in the presence of acetone, and a further quantity (*b*) in the absence of acetone, only methyl alcohol being used as the extraneous solvent. In the former case, the same mixture of products was isolated, the chief of these being the compound, m. p. 110°, but in the latter case (*b*) an apparently homogeneous product was obtained, m. p. 108°, from ligroin; $[\alpha]_D^{18°}$ + 65·2° in water ($c = 1·038$), falling to 61·2° after 9 days; $[\alpha]_{5461}^{18°}$ + 77·0°, falling to 71·8° in 9 days (Found: C, 51·1; H, 7·6; OMe, 52·2. Calc. for $C_{10}H_{18}O_6$: C, 51·25; H, 7·7; OMe, 54·2%). This substance was obtained either as colourless plates or as long, transparent needles 1—2 cm. in length. Both forms had the same melting point.

When heated with phenylhydrazine, this product, which appeared to be the genuine tetramethyl γ-mannonolactone, gave a crystalline *phenylhydrazide*, m. p. 167° (from ether) (Found: C, 55·5; H, 7·6; OMe, 32·9; N, 8·4. $C_{16}H_{26}O_6$ requires C, 56·1; H, 7·6; OMe, 36·3; N, 8·2%). These analytical data suffice to show that the substance was the phenylhydrazide of a tetramethylmannonic acid.

γ-Mannonolactone-monoacetone.—γ-Mannonolactone was shaken with dry acetone containing a trace of hydrogen chloride (about 0·1%). Complete solution occurred in 20 minutes, and then the mineral acid was neutralised with silver carbonate. After filtration and evaporation, colourless crystals, m. p. 132°, were collected and also a second crop, m. p. 117° (impure diacetone derivative). Recrystallisation of the former product from acetone and ligroin gave colourless needles (yield, 85%), m. p. 133°; $[\alpha]_D^{20°}$ + 55·4° in water (c = 1·62) (Found: C, 49·1; H, 6·6. $C_9H_{14}O_6$ requires C, 49·5; H, 6·4%).

γ-Mannonolactone-diacetone.—Finely divided γ-mannonolactone (6 g.) was shaken with 400 c.c. of dry acetone containing 0·2% of hydrogen chloride. After 3 hours, when most of the lactone had dissolved, the mineral acid was removed with silver carbonate and the acetone evaporated under diminished pressure. Extraction of the crystalline residue with large volumes of light petroleum yielded colourless crystals, m. p. 122—125°; after recrystallisation from ligroin, m. p. 126°. $[\alpha]_D^{20°}$ + 50·6° in chloroform (c = 1); + 73·65° in 50% alcohol, falling to 45·9° after 20 days (Found: C, 55·8; H, 7·15. Calc. for $C_{12}H_{18}O_6$: C, 55·8; H, 7·0%). The melting point and physical constants agreed with those of γ-mannonolactone-diacetone observed by Ohle and Berend (*Ber.*, 1925, **58**, 2590) and the substance was identical with a specimen prepared by their method.

Dimethyl γ-Mannonolactone-monoacetone.—The above specimen of γ-mannonolactone-monoacetone was methylated by means of silver oxide and methyl iodide. The product crystallised from ether in bulky needles, m. p. 110°, and this was found to be identical with the product obtained above during the methylation of γ-mannonolactone in the presence of acetone (Found: OMe, 25·5. Calc.: OMe, 25·3%).

Dimethyl γ-Mannonolactone.—Hydrolysis of the above product with 0·1% aqueous hydrochloric acid gave a crystalline substance which crystallised from ethyl acetate–light petroleum in white needles, m. p. 109—110°; $[\alpha]_D^{20°}$ + 61·1° in water (c = 1·03), falling to 60·5° in 19 days. Yield, 60%. This was *dimethyl γ-mannonolactone* (Found: C, 46·6; H, 7·1; OMe, 28·9. $C_6H_{14}O_6$ requires C, 46·6; H, 6·8; OMe, 30·1%).

Tetra-acetyl γ-Mannonolactone.—A mixture of γ-mannonolactone

(1 g.), acetic anhydride (5 g.), and dry pyridine (6·7 g.) was shaken for 45 minutes until a clear solution was obtained, and this was kept in a stoppered vessel in the ice-chest for 2 days. After dilution with 50 c.c. of cold chloroform the solution was poured on powdered ice. The chloroform extract of this product was washed with water and sodium carbonate solution, dried, and evaporated. This gave a syrup which crystallised from ether in needles, m. p. 115—117°; the yield was 0·5 g. Recrystallisation from dry ether raised the m. p. to 120°. $[\alpha]_D$ + 44·9° in chloroform (c = 1·56) (Found: C, 48·6; H, 5·3. $C_{14}H_{18}O_{10}$ requires C, 48·55; H, 5·2%). This appeared to be the tetra-acetyl derivative of γ-mannonolactone.

Attempted Preparation of Derivatives of δ-Mannonolactone.—This crystalline substance, first described by Nef (*loc. cit.*) as β-mannonolactone, was prepared by Nef's method as modified by Hedenburg (*loc. cit.*). M. p. 162° (after recrystallisation from boiling ethyl alcohol); $[\alpha]_D^{20°}$ + 114·0° in water (c = 1·24), falling to + 27·5° after 21 hours. 20 G. of pure calcium mannonate gave 6·5 g. of this lactone.

This substance was treated with methyl iodide and silver oxide twice in the presence of methyl alcohol and once in the presence of acetone. The semi-crystalline product was drained on a tile and extracted with light petroleum, which removed a mobile liquid having $n_D^{18°}$ 1·4370. The crystals (m. p. 108°) showed no depression of m. p. in admixture with the specimen of tetramethyl γ-mannonolactone (Found: OMe, 52·2. Calc.: OMe, 54·2%). It thus appeared that the δ-lactone had been transformed into a γ-lactone during condensation with acetone which had been used as solvent in the methylation process.

Oxidation of Tetramethyl γ-Mannonolactone.—This crystalline lactone (1·5 g.) was heated with 13 c.c. of nitric acid (d 1·42) at 100° for about 15 minutes in order to initiate the oxidation. The bath was maintained at 95—100° for a further 7 hours, and the solution was then cooled and diluted, and the nitric acid removed as completely as possible by distillation under diminished pressure, followed by repeated dilution and further distillation. The syrupy residue, which contained crystals, was esterified with 4% methyl-alcoholic hydrogen chloride, and the product (0·85 g.) distilled under 0·1 mm.: Fraction I, from bath at 110—115°; 0·25 g., which crystallised immediately. Fraction II, bath at 115—120°; 0·4 g., which crystallised on nucleation with methyl dimethoxysuccinate. Fraction III, bath at 120—140°; 0·1 g., which was partly crystalline.

Fractions I and II were identical, since each gave on recrystallisation from light petroleum a crystalline ester, m. p. 68°, which was

identical with a specimen of methyl ester prepared from *meso*-tartaric acid, and this was confirmed by a mixed m. p. determination. The substance was therefore methyl *i*-dimethoxysuccinate (Found: C, 46·45; H, 9·6; OMe, 59·3. Calc.: C, 46·6; H, 9·6; OMe, 60·1%).

0·1 G. of this compound was converted into the methylamide by dissolving it in a saturated solution of methylamine in methyl alcohol. Crystals separated after 2 days, m. p. after recrystallisation 209°, giving no depression in admixture with *i*-dimethoxysuccinomethylamide prepared from *meso*tartaric acid by Haworth and Jones (*loc. cit.*) (Found: C, 47·1; H, 7·6; N, 13·1. Calc.: C, 47·1; H, 7·8; N, 13·7%).

Oxidation of Tetramethyl δ-Mannonolactone.—Crystalline 2 : 3 : 4 : 6-tetramethyl δ-mannonolactone (2·7 g.) prepared by the method described by Drew, Goodyear, and Haworth (this vol., p. 1243) was oxidised by digestion at 90° with 20 c.c. of nitric acid (*d* 1·42). The reaction proceeded smoothly, and after 4¼ hours the evolution of brown fumes had ceased and a colourless solution remained. After dilution the nitric acid was repeatedly evaporated at 40° in a vacuum with addition of water, and finally a syrup was obtained which was dissolved in 80 c.c. of methyl-alcoholic hydrogen chloride (3·5%) and digested at 70° for 6 hours. The cooled solution was neutralised with silver carbonate, and the ester obtained (2·3 g.) by the usual method of isolation. This distilled at 95—100°/0·07 mm. and showed $[\alpha]_D^{18°}$ − 27·3° (in water, c = 1·21). The ester gave on solution in methyl-alcoholic ammonia the crystalline amide, m. p. 255°. The ester was, however, identified by means of the following preparation of the crystalline methylamide.

The liquid ester (0·5 g.) was dissolved in methyl alcohol, and the solution was saturated with methylamine. Having been kept for 2 days, the solution was evaporated and gave a solid residue which was recrystallised from ethyl acetate. The first crop of crystals (0·14 g.) had m. p. 155—160° and obviously contained a slight impurity, which was removed on a further crystallisation from the same solvent. This gave a colourless, crystalline product (0·04 g.), m. p. 208—209°, identical with the specimen of *i*-dimethoxysuccinomethylamide prepared by Haworth and Jones from *meso*-tartaric acid. A second crop of crystals was obtained by concentrating all the mother-liquors; colourless needles (0·3 g.), m. p. 172°. This substance was recognised as *d*-arabo-trimethoxyglutaromethylamide, $[\alpha]_D^{18°}$ − 59·7° in water (c = 0·94), the enantiomorph of the *l*-variety described by Haworth and Jones (*loc. cit.*) as having m. p. 172°, $[\alpha]_D^{18°}$ + 59·9° in water (c = 1) (Found: C, 48·3; H, 8·3; N, 11·0; OMe, 36·3. Calc.: C, 48·35; H, 8·1; N, 11·2; OMe, 37·5%).

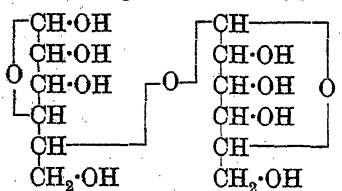
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NIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, October 27th*, 1927.]

CCCCXIII.—*The Constitution of the Disaccharides. Part XVII. Maltose and Melibiose.*

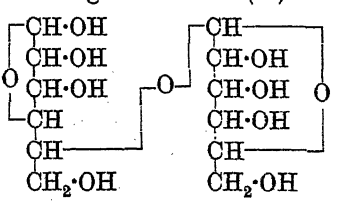
By WALTER NORMAN HAWORTH, JOHN VAUGHAN LOACH, and CHARLES WILLIAM LONG.

THE problem of the structure of maltose and melibiose has excited unusual controversy and various rival formulæ appear in the literature from time to time intended to supplant those submitted by one of us. The most recent of these attempts to reconstruct the constitution of these disaccharides is that made by Irvine in the published transcript of an address to the American Chemical Society (*Chemical Reviews*, 1927, 4, 203). Without contributingany fresh evidence, Irvine has now advocated the following scheme, wherein maltose is given formula (I) and melibiose is given formula (II) :



Glucose residue. Glucose residue.

(I.)



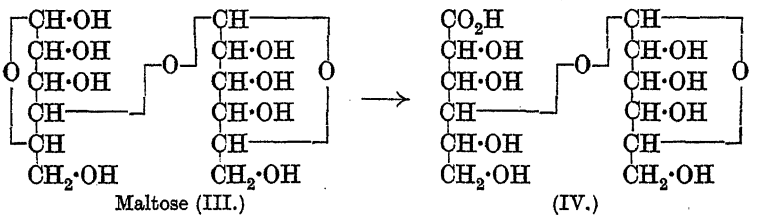
Glucose residue. Galactose residue.

(II.)

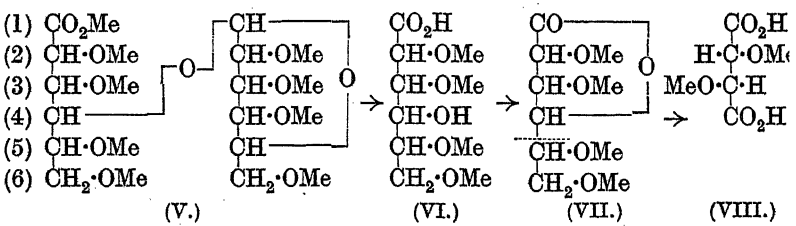
It is to be noticed that the revised structural form initially advocated by one of us for glucose in its normal derivatives is adopted for the non-reducing residue in (I), whilst the reducing glucose component in each disaccharide is given the character of a butylene oxide form which one of us applied to γ-glucose derivatives. Thus the effect of these new attempts to represent these disaccharides is to emphasise that each of them contains as its reducing hexose component a labile or γ-glucose residue. No evidence is given for the hypothesis that either maltose or melibiose is a γ-sugar, nor indeed do the properties of these disaccharides warrant that such an assumption need be entertained.

These views advanced by Irvine are indeed capable of simple and complete investigation, and in the case of maltose they have already been shown to be invalid by Haworth and Peat (J., 1926,

3094). The latter authors have demonstrated that maltose has the constitution (III), since it gives on oxidation a maltobionic acid which can only be formulated as in (IV). Completely methylated maltobionic ester (V) yields on hydrolysis only tetramethyl glucose and the tetramethyl gluconic acid (VI) which forms the γ-lactone (VII), and the structure of the latter has been proved by its oxidation to *d*-dimethoxysuccinic acid (VIII) and not to xylo-trimethoxyglutaric acid (Haworth, Hirst, and Miller, this vol., p. 2436), which is obtained from the corresponding tetramethyl δ-gluconolactone.



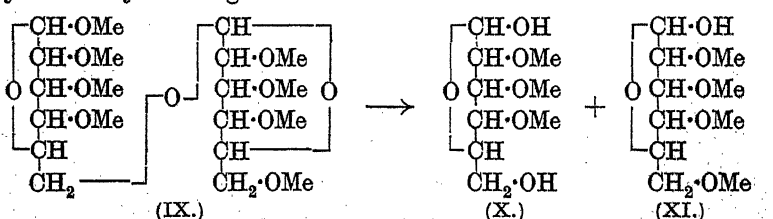
Maltose (III.) (IV.)



(V.) (VI.) (VII.) (VIII.)

These facts leave no room for doubt that the biose linking in maltose is situated at position 4 in the reducing biose. If this result is compared with that furnished by the isolation of 2 : 3 : 6-trimethyl glucose as a cleavage product of fully methylated maltose (Irvine and Black, J., 1926, 862; Cooper, Haworth, and Peat, *ibid.*, p. 876), the oxide ring of this hexose unit is seen to be present at the 5th carbon atom as shown in the maltose structure (III).

The case of melibiose is capable of a similar demonstration. Methylated melibiose (IX) yields on hydrolysis two cleavage products, one of which (XI) is crystalline, and the other, a liquid (X), yields a crystalline glucoside.



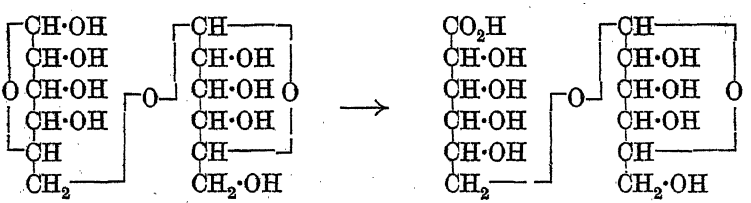
(IX.) (X.) (XI.)

2 : 3 : 4-Trimethyl glucose. 2 : 3 : 4 : 6-Tetramethyl galactose.

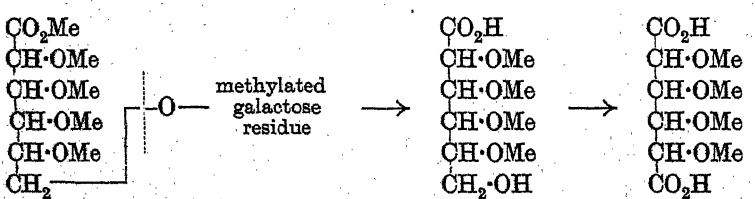
The inference was therefore drawn by Charlton, Haworth, and Hickinbottom (this vol., p. 1527) that the constitution (XII) should be allocated to melibiose, and the same formula was also supported by the earlier work of Haworth, Hirst, and Ruell on raffinose (J., 1923, **123**, 3125), and still earlier by Haworth and Leitch (J., 1918, **113**, 188).

This formula for melibiose is finally established by an alternative proof wherein melibionic acid (XIII) has been methylated to give methyl octamethylmelibionate (XIV), which on hydrolysis yields, besides crystalline 2 : 3 : 4 : 6-tetramethyl galactose, the 2 : 3 : 4 : 5-tetramethyl gluconic acid (XV) which does not form a lactone. The structure of the latter product has been determined by its oxidation with nitric acid to tetramethylsaccharic acid (XVI), which gives a crystalline methyl ester identical in every respect with that obtained by methylating saccharic acid.

It is therefore demonstrated that since 2 : 3 : 4 : 5-tetramethyl gluconic acid (XV) is the only product isolated which corresponds to the glucose component of melibiose, this component is attached to the galactose residue through the hydroxyl in position 6.



Melibiose (XII.) (XIII.)



(XIV.) (XV.) (XVI.)

The structural formula assigned by one of us to melibiose (XII) thus receives substantial confirmation from these new experimental results, as does also our formula for raffinose.

Another aspect of the constitution of this disaccharide is the stereochemical signification given to it in the current literature as a glucose-β-galactoside, a conclusion based on the observation that melibiose is said to undergo slow hydrolysis with emulsin (Fischer and Armstrong, *Ber.*, 1902, **35**, 3144). Helferich and

Rauch, however, have synthesised a biose of this configuration and structure, and the specific rotations both of the sugar and of its octa-acetate indicate its non-identity with melibiose (*Ber.*, 1926, **59**, 2655). Other considerations serve to show also that the stereochemical characterisation of this sugar revealing the presence of a β-biose junction between the two hexose residues is unsound. This has been argued in a previous paper (Charlton, Haworth, and Hickinbottom, *loc. cit.*) wherein it is suggested that melibiose may be a glucose-α-galactoside corresponding to maltose, which is a glucose-α-glucoside.

The argument may be supplemented by the new data now made available in the present experimental work. The methylated esters of the monobasic acids corresponding to each of the disaccharides, maltose, cellobiose, lactose, melibiose, have been prepared and their specific rotations are given, and in addition the rotation changes consequent upon their hydrolysis to the constituent hexoses and hexonic acids have been recorded. Each of these methylated esters may be regarded, for the purpose of comparison, as the equivalent of a methylglucoside or a methylgalactoside which may be recognised either as an α- or a β-form. In the case of the simple methylhexosides the magnitude of rotation alone is accepted as a sufficient indication of stereochemical homogeneity. If the analogous principle be conceded also for the methylated esters of the various bionic acids, the data now collected may be valuable evidence of the stereochemical nature of the bionic junction between the gluconic acid residue and the remaining hexose in a bionic acid, and, by inference, of the character also of the biose junction in the parent disaccharide. It may be mentioned that methylation of α-methylglucoside, etc., does not appear materially to effect interchange into the β-methylglucoside.

	$[\alpha]_D$.		Equilibrium attained on hydrolytic cleavage.
(1) Methyl octamethylmaltobionate ...	+121°	→	+54·9°
(2) Methyl octamethylcellobionate ...	+ 5	→	+55
(3) Methyl octamethyl-lactobionate ...	+ 34	→	+77·2
(4) Methyl octamethylmelibionate ...	+106	→	+64

The significance of these figures is the comparatively small magnitude of rotation of the substances Nos. 2 and 3, which are the products from the authenticated β-bioses, namely, cellobiose, which is glucose-β-glucoside, and lactose, which is glucose-β-galactoside. It may be further observed that these low rotation values show an increase when the ester is hydrolysed to the constituent hexose and hexonic acid. The equilibrium rotation value of the hexose is known already from previous experiments, whilst the specific

rotations of the methylated hexonic acids are also known (Drew, Goodyear, and Haworth, this vol., p. 1237).

	$[\alpha]_D$.
Tetramethyl glucose	84° (at equil.)
,, galactose	+117 (at equil.)
2 : 3 : 5 : 6-Tetramethyl gluconic acid	+ 27
2 : 3 : 4 : 5- ,, ,, ,,	+ 10

Inspection of the figures available for cases Nos. 1 and 4 reveals a striking similarity between these two derivatives of maltose and melibiose, inasmuch as both the esters have initially a high specific rotation which declines to a lower value on hydrolysis. The inference which might be drawn is therefore that in each of these examples the α-linking of a glucoside is undergoing cleavage to the hexonic acid and to the α + β-equilibrated mixture of the methylated hexose.

If this evidence be considered to provide a valid argument for the case of melibiose, it will then be clear that this disaccharide is not a glucose-β-galactoside, which is the view commonly accepted on the basis of Fischer and Armstrong's observation, but is a glucose-α-galactoside.

Discussion of Results.

With the present work there is now concluded a survey of the constitution of the six commonly occurring disaccharides—sucrose, cellobiose, maltose, gentiobiose, lactose, and melibiose—and the structural classification of these may now be reviewed in the light of these new data, and of the controversy which these and the earlier results of one of us and his collaborators has excited.

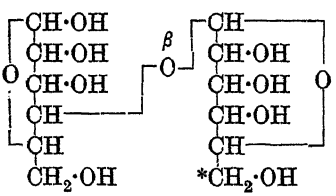
Chief among these criticisms have been those of Irvine in earlier papers (J., 1926, 867, 1506), but his more mature views appear to be concentrated in his recent article in *Chemical Reviews* (*loc. cit.*). The following extract from this article may be quoted: "In the structural classification of the disaccharides built up by Haworth" "this important issue* has been entirely overlooked," and "in addition, it is now recognised that his work involves a fundamental experimental error which renders his whole scheme valueless and that consequently, so far as the constitution of the disaccharides is concerned, we are only at the beginning of things in place of at the end."

Whilst affirming this belief, Irvine then proceeds to "turn to

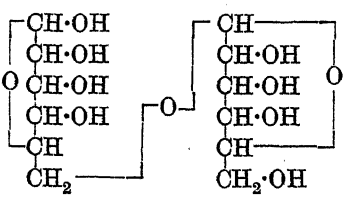
* Far from having been overlooked, this issue originated in a clear, cautious statement by one of us (J., 1926, 98, footnote) and it was there considered to be a possible though unlikely contingency, a view since justified in that it has been shown not to arise in any of the cases for which it was entertained.—W. N. HAWORTH.

the authentic results obtained," but instead of giving here only examples initiated by his own experimental work he quotes in detail, in the cases of no fewer than four of the six disaccharides, the experimental results and formulæ copied from our original papers published before he gave his address to the American Chemical Society (see *Chemical Reviews*), and in so doing he suppresses all reference and acknowledgment to the original authors.

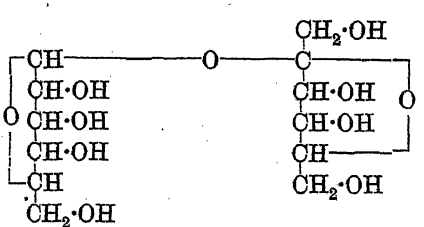
Irvine is committed to the advocacy of all but two of the constitutional formulæ for disaccharides initiated by one of us. The following are the formulæ quoted by Irvine in detail; these conclusions are identical with those previously given by Haworth and Hirst (J., 1921, **119**, 193), Haworth and Leitch (J., 1918, **113**, 188), Haworth and Wylam (J., 1923, **123**, 3120), Charlton, Haworth, and Peat (J., 1926, 89), and Haworth and Hirst (J., 1926, 1858).



Cellobiose (when both hexoses are glucose).
Lactose (when the hexose * is galactose).



Gentiobiose.



Sucrose.

The allocation of the above formula to sucrose was dependent upon, and could only have been made simultaneously with, the disproof and abandonment of Irvine's butylene oxide formula for normal fructose derivatives, since it is this formula which Haworth and Hirst then assigned (July, 1926) to the γ-fructose component in sucrose (compare subsequent paper by Avery, Haworth, and Hirst, this vol., p. 2308).

For the constitutions of the remaining two disaccharides, maltose and melibiose, against which the main criticism is evidently directed, Irvine has contended for the expressions (I) and (II) quoted already on p. 3146. The purport of the present communication is to demonstrate that in these two examples Irvine's formulæ are

erroneous, as is also his formula for raffinose, and it thus appears that in none of the six cases has a disaccharide formula been initiated by Irvine which has survived. The latter author has assigned, however, structural formulæ to cello*iso*biose and to the *iso*maltose of starch, although no experimental evidence accompanies these views and most workers, including the discoverers of these bioses, would do little more at this stage than postulate the probable existence of these two disaccharides (compare Haworth, *J. Soc. Chem. Ind.*, 1927, **46**, 295).

Experimental.

Oxidation of Melibiose to Melibionic Acid.—Melibiose (28 g.) having the recognised constants and having been prepared from pure raffinose was agitated with 210 c.c. of water to which were added in portions at intervals 16 c.c. of bromine, and the mixture was kept at about 20° with frequent agitation during about 7 days; then it appeared no longer to reduce Fehling's solution. The solution was then aerated, treated with hydrogen sulphide, and again aerated. Powdered litharge (50 g.) was added, and the mixture shaken for 4 hours until all the mineral acid present had been neutralised. The filtrate and the washings from the lead salts were shaken with finely divided silver oxide and the mixture was kept in the dark for some time. It was then filtered, treated with hydrogen sulphide, and again filtered, and the filtrate was evaporated and digested with precipitated calcium carbonate (10 g.). The filtrate and washings from this treatment were treated with charcoal and evaporated to a volume of 50 c.c. This solution was poured slowly with stirring into about 2 litres of methylated spirit. The precipitated, slightly glutinous solid was placed in contact with fresh methylated spirit and stirred until a hard granular product was formed. This was collected and dried in a vacuum, appearing as an almost white powder which was calcium melibionate. A further quantity of this calcium salt was recovered from the methylated spirit by evaporation, and purified as before by pouring into a fresh lot of methylated spirit. The dried calcium salt was devoid of action towards Fehling's solution. Yield, 92%. The calcium estimation showed Ca 4·74%. It thus appeared that the solid contained either two or three mols. of ethyl alcohol.

Methylation. Calcium melibionate (20 g.) was methylated in the usual manner with methyl sulphate in presence of sodium hydroxide, and the product was submitted to two similar treatments. The methylation process was completed by the use of Purdie's reagents, which were employed initially in presence of

a little water and finally the dry reagents were employed. The crude product resulting from this treatment contained OMe, 53·9%. It was then distilled under 0·05 mm., and the small amount (1·4 g.) of distillate collected below a bath temperature of 190° was rejected. The remaining portion of the distillate (12·5 g.) was collected at a bath temperature of 200—210°, and this on redistillation had b. p. 173 –175°/0·06 mm.; $n_D^{14°}$ 1·4640; $[\alpha]_D^{13°}$ + 106·4° in water (c = 1·63) (Found: C, 51·9; H, 8·5; OMe, 54·5. $C_{21}H_{40}O_{12}$ requires C, 52·1; H, 8·3; OMe, 57·65%). The product thus appeared to be essentially methyl octamethylmelibionate.

Hydrolysis. The above product was digested in a bath at 90° with a 7% solution of hydrochloric acid, and polarimetric readings were taken during the process of hydrolysis. The observations were taken by interrupting the course of the hydrolysis, removing a small sample and cooling, and these observations were continued until a constant rotation was obtained. $[\alpha]_D^{20°}$ + 106·1° (initial), 99·6° (after 30 mins.), 89·6° (60 mins.), 81° (90 mins.), 73·4° (120 mins.), 64·0° (180 mins.). After the solution had been kept overnight, the reading was + 64·3°, and it was ascertained that this reading remained constant after further heating. The mineral acid was then neutralised with barium carbonate, air being drawn through the solution at 50° to assist the neutralisation. The faintly coloured filtrate was treated with charcoal until quite colourless and evaporated at 40° in a vacuum. The residue was thoroughly dried by mixing it with acetone and removal of solvent, and finally by heating in a vacuum; the white residue thus obtained was extracted many times with boiling ether. The collected extracts yielded a syrup which crystallised on keeping. It was ascertained that this was 2 : 3 : 4 : 6-tetramethyl galactose (yield, 96·2% of the theoretical). The crystals were drained on porous tile and purified from light petroleum; m. p. 71—72°; $[\alpha]_D^{21°}$ + 117·8° (equilibrium). A mixed m. p. determination with an authentic specimen of 2 : 3 : 4 : 6-tetramethyl galactose proved its identity.

Again, 1 g. of the crude sugar was heated with 3 c.c. of aniline and 30 c.c. of ethyl alcohol during 5 hours. The crystalline tetramethyl galactose anilide separated and was recrystallised from ethyl acetate (yield, 92%); m. p. 192—193°, mixed m. p. determination with an authentic specimen prepared from lactose, 192—193°.

The residue remaining after the ether extraction of the tetramethyl galactose contained a barium salt of an organic acid. This was dissolved in water and treated with the equivalent of dilute hydrochloric acid to liberate the whole of the organic acid. The solution was completely evaporated at 30° in a vacuum and finally

at 35—40°. The residue was thoroughly dried by adding acetone and evaporating the solvent and finally by heating in a high vacuum at 70°. It was then extracted repeatedly with ether and the collected extracts were evaporated, yielding 4·2 g. of a tetramethyl gluconic acid (yield, 86·8% of the theoretical). The latter distilled under 0·05 mm. very slowly from a bath at 164°, giving a colourless, highly viscid syrup, which gave analytical figures pointing to its having been converted during this operation into an anhydro-form by condensation of two molecules (Found: C, 49·5; H, 8·0; OMe, 48·6. $C_{20}H_{38}O_{13}$ requires C, 49·4; H, 7·8; OMe, 51·0%).

The above undistilled acid (1 g.) was now oxidised in contact with 10 c.c. of nitric acid (*d* 1·2). Nitrous fumes began to be evolved at 75°. The temperature was gradually raised to 100°, and the solution maintained at this temperature for 5 hours. On removal of the nitric acid in a vacuum by repeated evaporation, accompanied by the intermittent addition of water, a liquid acid product was obtained. This was esterified with methyl-alcoholic hydrogen chloride (3%). Removal of the mineral acid was effected with silver carbonate and the filtrate was treated with charcoal to eliminate colloidal silver. A colourless liquid product (0·95 g.) was obtained on evaporation of this solvent. This was distilled under 0·09 mm. from a bath heated at 116—119°, and gave 0·8 g. of a colourless mobile liquid which crystallised during the distillation. This solid was recrystallised from dry ether, in which it was very soluble, giving hexagonal prisms, m. p. 77—78°. These were identical with the crystalline methyl tetramethylsaccharate which was prepared for the purpose of comparison by the methylation of saccharic acid. Karrer and Peyer (*Helv. Chim. Acta*, 1922, **5**, 577) also have prepared methyl tetramethylsaccharate from saccharic acid and they give m. p. 68°. By repeating the preparation of these authors, we also observed m. p. 68—71° for the partly purified material, but after three recrystallisations from ether the m. p. was raised to 76—77°. This preparation of the ester and of its derivatives will be described in a subsequent paper by Haworth and Jones. Mixed m. p. determination with the specimen isolated *via* melibiose, 77—78° (Found: C, 49·1; H, 7·2; OMe, 63·5. $C_{12}H_{22}O_8$ requires C, 49·0; H, 7·5; OMe, 63·3%). The diamide was also prepared: hexagonal plates (from water), m. p. 237—239° (Found: C, 45·4; H, 7·7; N, 10·7. Calc.: C, 45·4; H, 7·65; N, 10·6%).

The tetramethyl gluconic acid isolated as a cleavage product of methyl octamethylmelibionate is thus seen to be 2 : 3 : 4 : 5-tetramethyl gluconic acid, since it gives the tetramethylsaccharic acid on oxidation of a terminal $-CH_2\cdot OH$ group.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, November 17th*, 1927.]

CCCCXIV.—*Ionisation and Chemical Change during Slow Combustion.*

By JAMES ALLAN JAMIESON BENNETT and ERNEST WALTER JOHN MARDLES.

DURING the period of slow combustion, important changes occur in a gas mixture rendering it sensitive to inflammation. Bone, Fraser, and Witt have recently demonstrated (*Proc. Roy. Soc.*, 1927, *A*, **114**, 442) that with mixtures of methane and oxygen when an electric spark is passed there is a definite lag or induction period before main combustion occurs. Ionisation has sometimes been detected during the slow combustion of a hydrocarbon, alcohol, etc., in air, and is associated with the formation of a fine mist (Bennett, *Trans. Faraday Soc.*, 1927, **23**, 295).

It has been found that a system containing liquid droplets is more ionised and more sensitive to ignition than the corresponding vapour mixture. Many different mixtures of *n*-hexane and air have been passed through a horizontal glass tube, heated in an electric furnace to 675°, without ignition occurring, but if the tube was tilted or held vertically, a fine mist passed back against the stream and then ignition often occurred as low as 550°. When hexane was sprayed down the tube ignition occurred at 570°. A similar behaviour was observed with a number of substances, as shown in Table I. The apparatus employed was the same as described by Callendar (*Engineering*, 1927, **123**, 147) and Bennett (*loc. cit.*); and the spontaneous ignition temperature given is the minimum observed on varying the mixture strength. The rate of flow through the tubes was the same for both spray and vapour.

TABLE I.

Spontaneous ignition temperatures of vapour or spray of some liquids in air; heated-tube method.

Substance.	Spray.	Vapour.
m-Xylene	610°	710°
n-Butyl alcohol	635	725
Undecane (b. p. 198—208°)	506	550
Benzyl alcohol	546	571
Amyl ether	516	591
Cymene (b. p. 174—176°)	571	606

The minimum ignition temperature obtained with a falling temperature was often much lower than with a rising temperature. Thus, with a mixture of acetylene and air a sharp explosion first occurred at 340° with a rising temperature, but on lowering the temperature the mixture continued to catch fire at intervals even below 300° without violence, indicating that something remained in the tube from the previous combustion which rendered the fresh gas mixture sensitive to ignition.

Chemical changes occur below the ignition temperature, and these were usually more marked and occurred at lower temperatures with the liquid drops present than with the vapours alone. Thus with cymene at 370° the aldehyde and peroxide tests were given by the liquid drops but not by the vapour; lime-water was turned milky at 425° by the products from the spray, but it was necessary to raise the temperature to 440° in the case of the vapour before the presence of carbon dioxide could be definitely demonstrated. Table II gives some results obtained with a spray in quartz tubes with light from the mercury-vapour lamp. The electrical conductivity was measured in the manner described by Bennett (*loc. cit.*).

TABLE II.

Chemical and ionisation changes during the slow combustion of (*a*) cymene; (*b*) amyl ether; (*c*) undecane.

	Temp.	Observations.
(*a*)	275°	Aldehyde and peroxide tests given.
	300	Fog formed; slight ionisation.
	400	Dense, white fog, with pronounced ionisation; carbon dioxide present.
(*b*)	120	Aldehyde and peroxide tests given.
	300	Slight ionisation; white fog formed.
(*c*)	150	Aldehyde and peroxide tests given.
	275	Slight ionisation; white fog formed.
	450	Pronounced ionisation; dense white fog and nearly complete combustion of undecane to aldehydes, acids, CO_2, etc.

Although the high degree of ionisation is regarded as an accompaniment of, rather than as the direct cause of, detonation in the internal-combustion engine (Symposium on Gaseous Reactions, *Trans. Faraday Soc.*, October, 1926), yet the important rôle that can be played by electron emission follows from Callendar's nuclear-drop theory, the electron being capable of acting as a nucleus (Aeronautical Research Committee, R. and M. 1013, H.M.S.O.).

The coincidence of mist formation and ionisation during the slow combustion of a large number of substances raised the question as to whether ionisation was due to the development of surface (compare Simpson, *Phil. Trans.*, 1909, *A*, **209**, 379) or whether it was

the result of chemical change, and this matter is under investigation.

Although it is not certain whether all gaseous reactions are accompanied by ionisation (compare Trautz and Henglein, *Z. anorg. Chem.*, 1920, **110**, 257), the results shown in Table III indicate that at higher temperatures slight ionisation occurs with some mixtures. Moreover, Brewer (*Proc. Nat. Acad. Sci.*, 1926, **12**, 560) has observed ionisation during the catalytic oxidation of a number of organic substances, *e.g.*, xylene, acetone, etc.

TABLE III.

Mixture with air.	Composition (% by vol.).	Temp. of initial combustion.	Temp. when slight ionisation first observed.
Carbon monoxide	48·5	465°	500°
„ „	9·0	460	460
Carbon monoxide and hydrogen	22% CO, 11% H_2	430	430
Hexane	5	350	650
Ethyl ether	10	173	400

In no case was ionisation observed below the temperature of initial oxidation, *i.e.*, when aldehydes were first detected, and usually only slight ionisation was observed at higher temperatures even when oxidation was extensive. This delay might appear to throw some light on the mechanism of chemical reaction during the combustion of hydrocarbons. The scission of the oxygen molecule into atoms would probably result in profuse liberation of electrons so that hypotheses of oxidation and combustion at moderate temperatures which involve this atomic separation (*e.g.*, the hydroxylation theory) are not so convincing as those in which the oxygen molecule is regarded as being incorporated as a whole, *i.e.*, when O = O becomes — O — O — in the formation of peroxides from hydrocarbons:

$$R{\cdot}CH_3 + O_2 \rightarrow R{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}H; \quad >C{:}C< + O_2 = >C\overset{O-O}{\underset{O-O}{}}C<.$$

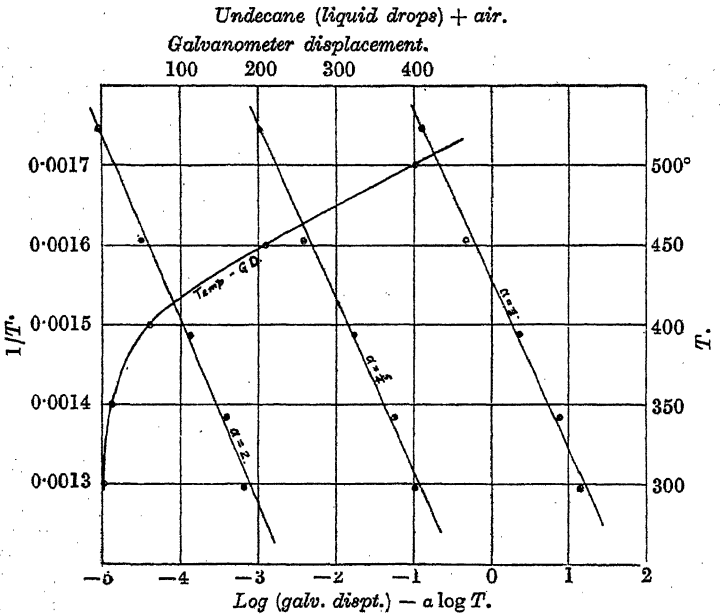
The formula $i = \theta T^{\alpha} e^{-\phi/T}$ (where $\alpha = \frac{1}{2}, \frac{5}{4}$, or 2; i = current; T = temperature; and θ and ϕ are constants) satisfies cases of thermionic emission, ionisation in flames, and ionisation in liquid drops–air systems during slow combustion, since in each case, within the limits of experimental error, all points plotted with axes (log $i - \alpha \log T$) and $1/T$ fall on straight lines (Bennett, *loc. cit.*).

The rate of chemical action, dc/dt, is expressed by the above equation if $\alpha = \frac{1}{2}$ and $i = dc/dt$. Richardson concluded that since ϕ in the case of chemical action differs from that in the case of thermionic emission the emission cannot be due to chemical action, but Brewer (*loc. cit.*) has now accounted for this difference.

In the light of these conclusions it seems probable that the pro-

cesses occurring at the beginning of and during combustion are (*a*) a thermionic emission and (*b*) the formation of centres of chemical change from ions as soon as they are liberated (compare Lind and Bardwell, *J. Amer. Chem. Soc.*, 1926, **48**, 2335).

FIG. 1.



Action of Iron Carbonyl, Lead Tetraethyl, Aniline, etc., on Slow Combustion and Ionisation.

The presence of iron carbonyl, lead tetraethyl, etc., even in small quantities exerts a great influence on slow combustion, delaying spontaneous inflammation and altering the temperature at which appreciable combustion begins. Some results are given in Tables IV and V.

TABLE IV.

The influence of lead tetraethyl and iron carbonyl on spontaneous ignition temperature.

Substance, spray in air.	Spontaneous ignition temp.
m-Xylene	610°
„ plus 0·3% (vol.) lead tetraethyl	650
„ „ 0·5% (vol.) lead tetraethyl	688
„ „ 1·0% (vol.) iron carbonyl	700
n-Butyl alcohol	635
„ „ plus 1% (vol.) lead tetraethyl	687

TABLE V.

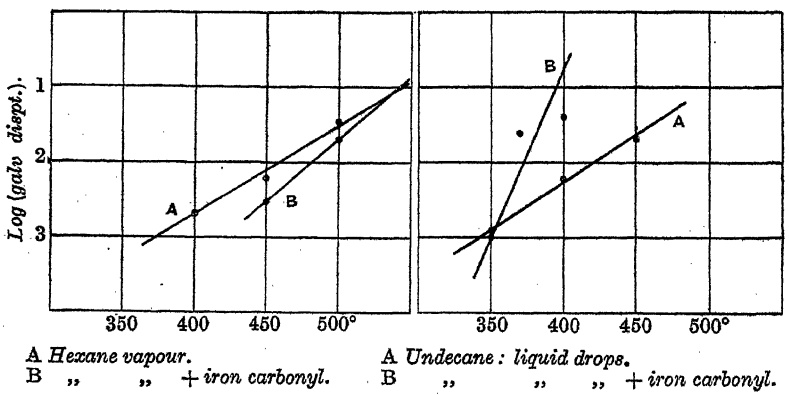
The influence of iron carbonyl, lead tetraethyl, etc., on chemical change and ionisation during slow combustion.

Substance.	Temp. of initial combustion.*	Ionisation.
Undecane, spray in air	200°	Very slight at 275°.
„ plus 0·2% iron carbonyl	238	Not detected until 330°.
„ „ 0·5% lead tetraethyl	305	Less than with undecane alone, below 350°.
„ „ 20% *m*-toluidine	248	The same as with undecane.
„ „ 20% *m*-xylidine	275	„ „ „
„ „ 20% *m*-cresol	310	Not detected until nearly 400°.
„ „ 20% carbon disulphide	230	„ „ „

* *I.e.*, as measured by the appearance of aldehydes.

The action of iron carbonyl, lead tetraethyl, and other "anti-knockers" appears to be the inhibition of peroxide formation during

FIG. 2.



A *Hexane vapour.* B „ „ + *iron carbonyl.*

A *Undecane: liquid drops.* B „ „ „ + *iron carbonyl.*

the period of slow combustion (Callendar, *loc. cit.*), and although below a temperature of about 400°, iron carbonyl and lead tetraethyl reduce the rate of chemical change, yet at higher temperatures there is a higher yield of water and carbon dioxide. This is shown in Table VI.

It will be seen from Fig. 2 that the ionisation curves for a very rich mixture of hexane and a spray of undecane containing iron carbonyl cross those for the "undoped" fuel, indicating that the initial decrease in chemical change is accompanied by a decrease in electron emission, whilst increased ionisation at higher temperature results from increased combustion, probably at the surface of the metal particles produced by the thermal decomposition of the metallic compounds.

TABLE VI.

The influence of lead tetraethyl on the quantity of carbon dioxide in the oxidation products of *n*-hexane at different temperatures.

	% CO_2 in oxidation products,	
Temp.	without lead tetraethyl.	with about 0·25% lead tetraethyl.
265°	Trace	Nil
300	2·1	Trace
400	1·9	3·3

Experiments with hydrogen, and with hydrogen–air, hexane–air, coal-gas–air, and acetylene–air mixtures, with and without puffs of iron carbonyl, lead tetraethyl, and nickel carbonyl, were made at temperatures up to 600°, and usually the addition of the organometallic compound was found not appreciably to increase ionisation. By a special device, only a trace of iron carbonyl, etc., was allowed to enter the stream of gases, and then only for a few seconds while the reading was being taken. With carbon monoxide–air mixtures there was a rapid movement on the galvanometer scale as the "doped" gas mixture passed across the electrodes, followed by a return to the normal reading after the puff had passed. The fouling of the electrodes and tube caused much difficulty in measuring the ionisation, and they had frequently to be thoroughly cleaned during the experiments.

The mixture (67% CO + 33% H_2)–air gave very striking results. As a puff rich in iron carbonyl was passed through the combustion tube at 500° along with the mixture, the current passing between the electrodes increased approximately 2000-fold. The actual readings were :

Temp.	Galvanometer displacement (mm.).	Remarks.
430°	3	Without $Fe(CO)_5$.
500	25	"
500	450 (with shunt, 100)	With $Fe(CO)_5$.
500	35	After passage of puff.

It will be noticed that (1) after the puff had passed through the tube the conductivity decreased to its former order of magnitude, (2) there was a slight persistence of increased conductivity, (3) the galvanometer reading did not increase suddenly, but at first it moved gradually and then rapidly accelerated till, when the spot had reached the end of the scale, its velocity was very great. The state of ionisation tends to remain unchanged.

Some typical results with the less effective mixtures are given in Table VII.

A mixture of air and iron carbonyl was passed through the combustion tube and did not cause any movement of the galvanometer.

TABLE VII.

Mixture.	Strength of mixture.	Temp.	Galvanometer displacement (mm.).	Remarks.
CO plus air	Weak	520°	0	—
,, ,, ...	,,	600	2	—
,, ,, ...	,,	550	2	With lead tetraethyl.
,, ,, ...	,,	600	7	,, ,, ,,
Hydrogen–air ...	Rich	(335—650)	0	—
Iron carbonyl ...	,,	,,	0	—
Hydrogen plus air	50%	(525—600)	0	—
,, ,,	,,	,,	2	With lead tetraethyl.
,, ,,	,,	,,	5	With iron carbonyl.
,, ,,	10%	(450—570)	40	With lead tetraethyl.
Coal-gas–air	50%	610	10	—
,, ,, ...	,,	,,	20	With iron carbonyl.
Acetylene–air ...	Weak	(150—470)	0	—
,, ,, ...	,,	470	1	With nickel carbonyl. On addition of iron carbonyl, temp. of electrodes rose suddenly to 800° and mixture exploded.
,, ,, ...	,,	500	—	

The addition of a puff of the hydrogen–carbon monoxide mixture increased the conductivity to a high degree, as described before. The temperature was not increased by the puff and it must therefore be concluded that the ionisation was due to chemical change.

The characteristic action of lead tetraethyl and iron pentacarbonyl on the slow combustion of the gases mentioned was to delay spontaneous ignition and to lower the temperature at which slow combustion began by 50—100°. However, at 600° the amount of oxidation of carbon monoxide was not appreciably affected by the presence of small amounts of these substances.

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AIR MINISTRY LABORATORY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W. 7.

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NOTES.

Pregl's Universal Filling applied to Macro-combustions. By WILLIAM DAVIES.

THE filling used in Pregl's method ("Die Quantitative Organische Mikroanalyse," 1923) of carbon and hydrogen determination has now been applied successfully on a macro-scale, and as such a universal filling has many advantages, the method is briefly indicated.

An ordinary combustion tube of about 1·2—1·5 cm. internal diameter and 95—100 cm. long is used. A plug of silver wool or silver gauze (1·5 cm.) precedes the filling of mixed copper oxide (wire form) and lead chromate (about 43 cm.); this is followed by a mixed

silver wool and asbestos plug (2·5 cm.), and finally by a filling of lead peroxide asbestos (about 13 cm.). The last is prepared after Pregl (*op. cit.*, p. 29), but the thorough drying of this material on a large scale offers some difficulties, for the temperature at which the peroxide begins to decompose is somewhat uncertain (100—290°; see Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VII, p. 687); that used in these experiments was dried in bulk at 200° for 4 hours, then spread out in shallow vessels and dried for 8 hours over calcium chloride at 100° under less than 30 mm. pressure, and finally heated before use for 3 hours in a rapid stream of air in the combustion tube at 180°. Even after this treatment a trace of moisture was still left, and the first value for hydrogen with a new tube was apt to be slightly high. The lead peroxide in the combustion tube is heated by a hollow boiler (15 cm. long and with a hole of 2·5 cm. diameter) made of brazed copper and is modelled on Pregl's "Hohlgranate." The "Kupferbügel" is best in the form of an almost cylindrical piece of copper (5 cm. long) which practically surrounds the combustion tube and is connected round the middle to the copper boiler by means of a thick copper rod. The boiler requires about 50 c.c. of liquid, and technical *o*-dichlorobenzene, b. p. 177—181° (corr.), is used. The furnace end of the boiler is provided with an asbestos ring which fits closely round the combustion tube, and the portion of the combustion tube in the boiler is loosely packed with asbestos. (For the construction of these boilers the author is indebted to Mr. J. L. Osborne.)

Owing to the much larger contact surface presented by the macro- as compared with the micro-filling, the Mariotte flask adopted by Pregl is discarded. Soda–lime and calcium chloride are used both in the purifying train and in the absorption tubes. The combustion is carried out in the ordinary way, care being taken not to heat too strongly that portion of the furnace immediately before the copper boiler. The silver filling and lead peroxide asbestos suffice for about 10 combustions.

The method has been thoroughly tested for many types of substances, including those containing halogens and sulphur, and both amino- and nitro-groups; representative analyses for such substances are: Chlorobenzene-2 : 4 : 6-trisulphonyl chloride (Found: C, 17·7, 17·7, 17·5; H, 0·9, 0·7, 0·6. Calc.: C, 17·6; H, 0·5%). Acetanilide (Found: C, 70·9, 71·1; H, 6·6, 6·5. Calc.: C, 71·1; H, 6·7%). *p*-Chloronitrobenzene (Found: C, 45·6, 45·5, 45·5, 45·8; H, 2·5, 2·5, 2·4, 2·6. Calc.: C, 45·7; H, 2·5%). 2 : 4-Dinitrotoluene (Found: C, 46·2, 46·0, 45·9; H, 3·2, 3·4, 3·4. Calc.: C, 46·1; H, 3·3%). Picryl chloride (Found: C, 29·1, 28·9, 29·1; H, 1·2, 0·9, 0·9. Calc.: C, 29·15; H, 0·8%).—MELBOURNE UNIVERSITY. [*Received, September 19th*, 1927.]

The Electroendosmosis of Aqueous Solutions through Glass Diaphragms. By HORACE CHARLES HEPBURN.

FAIRBROTHER and VARLEY (this vol., p. 1584) have measured the electroendosmosis of dilute hydrochloric acid through a diaphragm of sintered Jena " Geräte " glass powder, and their results lead them to conclude with Lachs and Kronman (*Rocz. Chem.*, 1926, 6, 641) that the interfacial equilibrium between glass and aqueous solutions is not a true one, but changes with time. They give the results of two series of electroendosmotic determinations with dilute hydrochloric acid, the second series consisting of a repetition of the first series after the diaphragm had been " carefully cleaned." In each series, the results were " quite concordant among themselves," but the electrokinetic potential was throughout less negative in Series II than in Series I. No reference is made to the lowering of electrokinetic potential produced by given concentrations of hydrochloric acid; when this factor is considered, however, the two series of results show a remarkable similarity. The lowering is given by $\zeta_0 - \zeta_c$, where ζ_0 and ζ_c represent the electrokinetic potential at concentrations zero and c, respectively; and values for $\zeta_0 - \zeta_c$, obtained from Fairbrother and Varley's results, are given in the subjoined table. It will be observed that, except in the case of the most dilute solution (where the potential lowering is small and the value is affected to a greater extent by experimental error), the two series of values are in satisfactory agreement.

	Lowering of electrokinetic potential (volt).	
Solution.	Series I.	Series II.
N/5000-HCl	0·0041	0·0075
N/1250-HCl	0·0113	0·0111
N/400-HCl	0·0163	0·0169
N/100-HCl	0·0310	0·0309

Thus, contrary to the view of Fairbrother and Varley, there appears to be little indication from these results of any change in the effective size of the diaphragm pores corresponding to a progressive swelling process at the glass surface; on the other hand, it seems probable that these authors, in the process of cleaning their diaphragm, failed to remove the last traces of adsorbed electrolyte. The difficulty in bringing a diaphragm back to its original state after treatment with an electrolyte solution has been referred to by Freundlich and von Elissafoff (*Z. physikal. Chem.*, 1912, 79, 385), who found, in some instances, that repeated treatment with concentrated nitric acid was necessary; similar treatment of a diaphragm of powdered glass, however, introduces the difficulty of removing the final traces of acid by washing with water. Fairbrother and Varley were able to reproduce the value of ζ obtained in the initial determination with water by treating the diaphragm

with nitric acid, but subsequent determinations with dilute hydrochloric acid gave results deviating from the original values.

The author (*Proc. Physical Soc.*, 1926, **38**, 363; 1927, **39**, 99) has surmounted the difficulty in bringing a diaphragm back to its original state after treatment with an electrolyte solution by employing an entirely fresh diaphragm for each series of observations. When this procedure was followed, it was possible to obtain concordant results in determinations made at intervals over a period of several months.—BIRKBECK COLLEGE (UNIVERSITY OF LONDON). [*Received, September 2nd*, 1927.]

The Use of Hydrogen Peroxide for Iodine and Other Substitutions in Aromatic Compounds. By JAMES ERNEST MARSH.

HYDROGEN peroxide may be used to facilitate substitutions. For example, a solution of phenol in alcohol with the calculated quantity of iodine is warmed and hydrogen peroxide (30%) is added, the colour of the iodine gradually disappears, and 2 : 4 : 6-tri-iodophenol crystallises. Similarly β-naphthol yields 1-iodo-β-naphthol in quantitative amount.

It is not necessary to start with iodine in the free state. When phenol is dissolved in glacial acetic acid, the requisite amount of potassium iodide added, and the solution heated, the addition of hydrogen peroxide brings about the quantitative separation of tri-iodophenol; replacement of the potassium iodide by a metallic bromide gives tribromophenol, and replacement by hydrochloric acid gives trichlorophenol.

The thiocarbimido-group can be introduced as follows: Dimethylaniline and potassium thiocyanate in molecular proportion are dissolved in glacial acetic acid and hydrogen peroxide is added gradually. The solution becomes hot and, on cooling, the compound $C_9H_{10}N_2S$ crystallises. It may be recrystallised from alcohol and forms colourless plates, m. p. 73° (Found: C, 61·0; H, 5·7; N, 15·7; S, 18·3. Calc.: C, 60·6; H, 5·6; N, 15·7; S, 18·0%). This compound was obtained by Söderbäck (*Annalen*, 1919, **419**, 275) by the action of an ethereal solution of thiocyanogen on dimethylaniline. It is probable that it is not a simple thiocyanogen derivative of dimethylaniline, but that it is identical with the compound which Schmidt synthesised (*Ber.*, 1906, **39**, 2409) by the action of nitrous acid on the condensation product of formaldehyde with *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid, and to which he assigned the constitution $NMe_2{\cdot}C_6H_3{<}\overset{S}{\underset{N}{>}}CH$.—UNIVERSITY MUSEUM, OXFORD. [*Received, October 28th*, 1927.]



A. W. CROSSLEY.

[*To face p.* 3165.]

OBITUARY NOTICES.

ARTHUR WILLIAM CROSSLEY.

BORN FEBRUARY 25TH 1869: DIED MARCH 5TH 1927.

ARTHUR WILLIAM CROSSLEY was born at Bentcliffe, Accrington, on February 25th 1869. His father, Richard Crossley, was a man of unusual qualities who after returning from America with ample means and losing the greater part, moved into Accrington in 1864 to make what amounted almost to a fresh start as manager to the firm of F. W. Grafton & Co., well known as calico printers. If Crossley owed his quiet, reserved disposition to his father, his tenacity and resolution were inherited from his mother, a Bissett of Aberdeen and a woman of remarkable energy and force of character. Of his boyhood little of interest can be recalled: it seems to have been uneventful and happy. From preparatory school he went in 1881 to Mill Hill—chosen for its nonconformist tradition—where he stayed until Easter 1885. The next three months were spent in Paris. In the following October he entered Owens College, but owing to an illness which caused the loss of a year, he did not obtain his Honours degree of B.Sc. until 1890.

After a session spent in Professor (now Sir Arthur) Schuster's laboratory, which led to the joint publication of a paper on the electro-deposition of silver (*Proc. Roy. Soc.*, 1892, **50**, 344), Crossley went to Emil Fischer at Würzburg in October 1891, stayed there until Fischer was translated to Berlin in succession to A. W. von Hofmann in the autumn of 1892 and remained with him in Berlin until the Christmas of that year. Before leaving Würzburg the degree of Ph.D. was conferred on him for his thesis entitled "I., Ueber die Oxydation einiger Dicarbonsaüren; II., Ueber das optische Verhalten des Dulcits und seiner Derivate."

Returning to Owens College early in 1893 to undertake research work with W. H. Perkin, junr., he was elected to a Bishop Berkeley research fellowship in the following year and became President of the College Union, revealing in the conduct of its affairs thoroughness and a sanity of judgment that later came to be recognised as characteristic. This admittedly was one of the happiest periods of his

life: he widened his social circle, was an active member of many college societies and, freed at last from the tyranny of examinations, gave regular hours to the cultivation of his singing voice—a baritone of fine quality and wide range. But for its uncertainty, he might have chosen the concert platform as a career rather than chemistry which, until devotion to experimental work came to possess him, was more his father's choice than his own. In April 1895 he was appointed teacher and demonstrator in physics and chemistry at St. Thomas's Hospital Medical School, where he succeeded Professor (now Sir Wyndham) Dunstan as chemical lecturer and consulting chemist in October 1900. Four years later he became Professor of Chemistry at the Pharmaceutical Society's School of Pharmacy, Bloomsbury Square. As the outcome of Crossley's research work at Owens College, two papers were published jointly with Perkin, the first in 1894 under the title "Substituted pimelic acids," (J., **65**, 987) and the second in 1898, nearly three years after his departure from Manchester, entitled "Decomposition of camphoric acid by fusion with potash or soda," (J., **73**, 1). Dihydrocamphoric acid, one of the products mentioned in the second paper, was the starting point of the series of investigations which occupied his attention until the outbreak of the War and led to the publication of some 40 papers in the Journal. With some of the early communications from St. Thomas's Hospital, the late Dr. H. R. Le Sueur was associated and in many of those from the School of Pharmacy, Miss Nora Renouf was his collaborator.

The earliest papers of the series dealt with attempts to synthesise $\alpha\alpha_1\beta\beta$-tetramethyladipic acid on the assumption that dihydrocamphoric acid had that constitution. Of the intermediates examined, 1 : 1 : 2-trimethyldihydroresorcin, obtained for the purpose by the condensation of mesityl oxide and ethyl sodiomethylmalonate, and 1 : 1-dimethyldihydroresorcin, its lower homologue, which had been made slightly earlier by Vorländer, proved so unexpectedly reactive that the original quest was abandoned. In its place, the detailed study of these hydroaromatic compounds and of their reduction, halogen and ketonic derivatives was pursued with ardour, leading as it did to the production of *o*-xylene derivatives by the migration of one of the members of the *gem*-dimethy group.

In the papers many indications of the care taken to check the occurrence and course of these transformations can be found. These led incidentally to the production of mono-, di- and tri-nitro-*o*-xylenes and to the preparation of all the isomeric forms of these substances. Further, a contribution to the loosening effect of nitro-groups

situated in the *ortho-* or *para*-position relatively to a given nitro-group arose out of the conversion of certain trinitro-*o*-xylenes into dinitro-*o*-xylidines by interaction with ammonia. And the emergence of halogenated *o*-xylenols in the later stages of the investigation showed the interest of the subject to be far from exhausted, when the War brought the work to an end.

Much attention was paid to the exact characterisation of hydrocarbons of the di-, tetra- and hexa-hydrobenzene series isolated in the course of the work, as troublesome obstacles were encountered owing to the frequent occurrence of mixtures of isomerides, closely similar in properties, in the synthetical products. As serving to connect these products with camphor and the terpenes, the synthesis of *iso*laurolene and of *cyclo*geraniolene may be noted. From the manner in which each experimental difficulty was attacked and solved, the whole investigation affords a good example of the art of scientific discovery.

It was especially during his tenure of the Chair at the School of Pharmacy, which lasted from 1904 to 1914, that Crossley found scope for the exercise of those qualities of organisation, tact and driving power which later were to be of inestimable service to the State. To him fell the completion of the scheme initiated by his predecessor for remodelling and re-equipping the Chemistry Department, aided as he was by the cordial co-operation of the veteran Michael Carteighe who, far-seeing and insistent, laboured to the end of his life for the advancement of the scientific side of pharmacy.

In his inaugural address at Bloomsbury Square, Crossley made it clear to the students that in his view pharmacy is "a great applied science" and also "a great profession" (*Pharm. J.*, 1904, **73**, 497). Imbued with this conception of the dignity of their calling, he set them a high standard of duty by the conscientious performance of his work as professor. No external interest, not even the fascination of research, was allowed to interfere with his weekly tour of the laboratory or that personal contact with each student to which he attached the utmost importance. But it was in his research laboratory—a curious, octagonal room, by no means well lighted or equipped for advanced work—that his devotion to chemistry found its outlet. There, too, by his example he inculcated thoroughness, careful observation and an ordered use of all laboratory hours, and, always open to suggestions or ideas from his fellow workers, he never failed to show appreciation of their share in bringing a research to a successful conclusion.

Naturally, all through this period, Crossley looked to a University Chair as his ultimate aim. When, therefore, he was appointed

Professor of Organic Chemistry in King's College, London, in June 1914, the wider opportunities for teaching and research that he coveted seemed at length to be his. But Fate willed otherwise. Within little more than a month, the Great War broke out and—save that he gave lectures during the session 1914/15 and returned to the College for a few months after the Armistice—his work as a Professor was done. Henceforward his energies were to be absorbed first in the country's defence and later in the effort for reconstructing industry that has followed the Peace.

Never one to wait, in an emergency, for employment fitting his attainments, Crossley in the earliest days of the War cheerfully undertook arduous clerical work as a volunteer in the War Office under Colonel (now Sir John) Pringle who was engaged in organising railway transport for troops in the Home Defence, Eastern Command and London District areas. Then, after aiding in the large-scale production of salvarsan under the name kharsivan, he became secretary of the War Committee appointed by the Royal Society to organise the production in universities and kindred institutions of local anaesthetics such as novocaine and β-eucaine and of other drugs hitherto obtainable only from enemy sources.

The bitter cry for shell in the spring of 1915 led to the establishment of the Ministry of Munitions. Of its Departments, that dealing with Trench warfare had for one of its functions the provision of all material required for the offensive in chemical warfare, rendered necessary by the introduction of gas as a weapon by the Germans on the western front on April 22nd of that year. As part of the organisation, two Committees termed Scientific Advisory and Commercial Advisory were set up in June * and of each Crossley was appointed secretary. The early days of chemical warfare were for him full of anxiety and incessant toil. The Scientific Advisory Committee sat almost continuously during each day; at night steps had to be taken to carry into effect its decisions. Crossley, as secretary, stood between the military in urgent need of new weapons the nature of which, perforce, they could not describe, and the Advisory Committee, faced with utterly new problems vitally important but requiring time, of which there was all too little, for their solution. In these early days, the contact between those in the fighting line and those working at home to provide the sorely-needed chemical weapons was small. To enable the latter to form some conception of the conditions at the front, Crossley was

* The Scientific Advisory Committee was a body of distinguished scientists charged with the duty of devising and investigating methods of prosecuting chemical warfare, the Commercial Advisory Committee a group of leading men in the British Chemical Industry in a position to advise upon and assist in the production of the necessary chemical materials.

given the additional appointment of Liaison Officer for Chemical Warfare in November 1915 with the rank of Lieutenant-Colonel and in this capacity made several visits to the battle areas in France.

Only slowly did the authorities at home realise that for the successful development of chemical warfare it was essential there should be available a large experimental ground where trials could be carried out on a scale approaching that of actual warfare. Space was required for testing under varying meteorological conditions both the methods of producing and the lethal or visual effects of toxic "gases" and smokes distributed from cylinders, by artillery fire, or otherwise. Eventually a large tract of bare land was acquired at Porton, east of Salisbury, and to Crossley in June 1916 was entrusted the task of converting it into a suitable experimental ground, of staffing and equipping it and of supervising the experimental work undertaken at the instance of the Army or the Committee. Thereupon, he ceased to be secretary of the Committee,* but was retained as a member and also as liaison officer.

How great the difficulties were and how he overcame them may be understood at least in part from the following appreciation most kindly furnished by Lieutenant-Colonel (then Major) R. M. Rendel, R.A., a regular officer who served under Crossley for two years—for the first three months as his adjutant and afterwards as one of his experimental officers.

"When Crossley arrived at Porton he found two small Army huts, each 30 feet by 15 feet, in the middle of Salisbury Plain, with no roads leading to them, no water, and no equipment of any kind. He was, with the exception of one subaltern R.E. and one warrant officer, quite alone. His first move was to get himself appointed to the military command of the Experimental Station; his second to collect the nucleus of a staff. By the end of June he had a chemical laboratory running in one of his Army huts, and by the end of the year detachments of Artillery and Engineers under their own officers had been posted to the Station. He was now in a position to begin the preliminary experiments, which were necessary for the solution of the hundreds of questions that had to be answered before the British Armies in the field could undertake chemical warfare.

"It would take too long to sum up the work done by Crossley

* The Scientific Advisory Committee was modified and re-named in successive reorganisations. Eventually it became the Chemical Warfare Committee, a body of enlarged constitution responsible for scientific investigations on the defensive as well as the offensive side of chemical warfare. Throughout its transformation and afterwards, Crossley continued to be a leading member.

during his two and a half years at Porton. It is doubtful whether anyone realises the immense volume of work actually achieved. Crossley himself wrote a summary for the War Records, a copy of which is filed at Porton, but it is both much too long and much too official to reproduce here. It may be of interest, however, to consider that at the time of the Armistice, little over two years after the beginning of the Experimental Station, Porton was staffed by 47 officers, 700 N.C.O.'s and men and 800 civilian workmen. Of the 47 officers roughly half were trained scientists, principally chemists and physiologists, several of them very eminent men. The two original Army huts had been replaced by large laboratories, workshops, gunsheds, magazines, barracks and canteens. Permanent roads were in existence over the ground; telephones, electric light, and water had been laid on. Large stores of shell, gas and so on, were situated on the ground and about 40 pieces of ordnance of all natures, from 9·2 howitzers downwards, and trench mortars of every description, were under Crossley's command. Over 40,000 rounds of ammunition had been fired, thousands of experiments had taken place and some of the results of Crossley's work had been embodied in over 800 reports. Chemical warfare was already highly developed.

"During those two years or more, from the moment Crossley came to the Station, work was carried on all day and during most of the night. Such was his driving power that lack of facilities never seemed to matter. It was one of Crossley's outstanding merits that, although he himself fully realised the difficulty of working without proper tools, yet he never allowed the lack of them to become an excuse for doing no work.

"Apart from the fact that it was wartime, work at Porton was carried on in a very pleasant atmosphere. There were no jealousies or bickerings between those engaged on the experiments. Whatever the differences of opinion between individuals, once a report had been issued it was always accepted as the official Porton view. It was always signed by Crossley, unless it were purely physiological, so that the Station did actually achieve an entity of its own. If reference were made to Porton, whether as regards some chemical question or as regards the functioning of a particular fuze, the reply was the Porton reply, the opinion the Porton opinion, the work was the work of Porton and Crossley signed the report. The physiologist was proud of the work done by the chemist, the chemist recognised the achievements of the gunner. A most valuable corporate feeling was thus created; it was entirely due to Crossley, and it was only possible because, while he always took responsibility for all that was said or done, he never took to himself credit

which was really due to others. All his staff were well aware of this.

"His position as commanding officer was a very real one. He was in actual military command of nearly 1,000 men, almost every one of whom had more military experience than he had. The type of man serving at Porton during the War was very good, but it is certainly to the credit of Crossley that serious military crime, both during the War and after the Armistice, was non-existent at Porton.

"He was the most hardworking of men. Sometimes severe, he very seldom praised; but he was absolutely fair-minded and all the time he was at Porton I never heard him criticised by any one of his staff. We were all devoted to him. Crossley was the best Commanding Officer I ever served under."

In September 1918, Crossley was appointed Daniell Professor of Chemistry and Director of the Chemical laboratories in King's College on the resignation of Sir Herbert Jackson, and after demobilisation returned to the college in October 1919. In common with many of those engaged in the big enterprises of the War, he found the routine of post-war days irksome, although with undiminished vigour he set himself to rebuild his department and revive academic research under the difficult conditions then prevailing. Soon the call came to him to undertake the organisation of the British Cotton Industry Research Association founded by the Lancashire cotton trade with the co-operation of the Department of Scientific and Industrial Research. Appointed Director on November 4th 1919, and leaving King's College in March 1920, it was on his recommendation that the house at Didsbury, now known as the Shirley Institute, was purchased. While it was being adapted to its new use and extended by the erection of a large block of laboratories and workshops, a beginning was made with cotton research in laboratories lent for the purpose by the University and by the Technical College in Manchester. To the Institute, the research staff was transferred early in 1922, the buildings being opened formally by H.R.H. the Duke of York on March 28th of that year. By the autumn of 1926, the research staff (including those of its members engaged in the workshops) which in 1921 numbered 28, had increased to 92 of whom 44 were university graduates. An account of some of the investigations in progress at the Institute formed the subject of a discourse given under the title "Science and the Cotton Industry," by the Director at the Royal Institution on Friday, January 23rd 1925.

In the autumn of 1923, the initial period of association with the Department of Scientific and Industrial Research drew to its close, and, although little more than a year of normal working had been

possible, the results were sufficiently encouraging to warrant a further grant of £45,000, spread over five years in a series of diminishing amounts, being made by the Department, on condition that the total annual income was raised to a minimum of £42,500. It was a source of much satisfaction to Crossley, and an unmistakable proof of confidence in his directorship that an industry hard hit as the cotton trade has been since the Peace, should shoulder the additional burden imposed by this condition. His aim was to make the Shirley Institute the brain of the chief industry of his beloved Lancashire, benefiting alike the cotton trade and all who depend on it for their living and prosperity. That, by his genius in planning and guiding research, he provided a sure foundation for ultimate success is evident from the review of the work of the Association to the end of 1926, recently published by the Shirley Institute under the title "Research in the Cotton Industry." Not improbably his work at Didsbury may come to be regarded as his best.

Crossley served the Chemical Society in many ways. He was an abstractor during the three years 1897–99 and a member of the Publication Committee for a period of twenty years ending in March 1926. From 1906, when he became Honorary Secretary, he held office without a break until his death, becoming Honorary Foreign Secretary in 1913, President in 1925 and on his resignation of the Chair, Vice-President in 1926.

The Annual General Meeting in 1926 was notable as being the first to be held out of London. Early in Crossley's presidency, the Council decided to make the experiment of holding the ensuing annual meeting in a provincial city. Most appropriately, Manchester was the city chosen, and the University the place of meeting. Crossley thus had the gratifying experience of occupying the Chair as President of the Society in the Chemistry lecture theatre in which he had sat as student under Roscoe and afterwards under Dixon, the latter of whom was present and took part in the proceedings. The presidential address was entitled "The Co-operation of Science and Industry," a subject constantly in his thoughts, to which he had also referred in a lecture on "Science and Industrial Problems" at the Royal Institution on February 5th 1915.

By nature Crossley was deliberate, but with his mind once made up resolute. Unfailingly courteous and genial to all in every relation of life, it is probable that comparatively few were admitted to the intimacy of his friendship. His recreations were typical: he played lawn tennis in his student days and golf later in life, but in billiards and fly-fishing—the latter absorbing entire holidays before the War—he found an abiding source of pleasure. To his culti-

vated taste books, of which at one time he was an eager collector, music and the theatre, made a strong appeal. Without being robust he enjoyed good health until the effect of the strain of the War years began to manifest itself. A voyage to Madeira in the May of 1925, after he had succeeded to the Presidency of the Society, gave a temporary respite, but in the autumn he was less well and early in January 1926 sought to resign office forthwith on medical advice. By relieving him of all work requiring his presence in London, the Council of the Chemical Society rendered it possible for the resignation to be deferred until the Annual General Meeting in March, thus enabling him to complete one year of office.

Before the summer was over, it was evident that his health was failing rapidly. Towards the end of the year he tendered his resignation of the Directorship of the British Cotton Industry Research Association, but by resolution of the Council remained nominally in office pending the appointment of a successor. This appointment had not been made and he was still Director when, on Saturday, March 5th, 1927, he died.

Crossley received many honours: D.Sc. (Victoria University) 1899; F.R.S. 1907; Hon. LL.D. (St. Andrews) 1917; C.M.G. 1917; Longstaff Medallist of the Chemical Society 1918; C.B.E. and Officier de la Légion d'Honneur 1919. In 1901 he married Muriel, daughter of Ralph Lamb of Liverpool, who with their son and daughter survived him. It may be permitted to add that the son, Kenneth Harwood Crossley, to the grief of all who watched his early career and had recognised his ability, tenacity of purpose and faculty for endearing himself to all with whom he worked, was drowned in a sailing accident off Llanddwyn Island, Anglesey, on July 30th, in his 23rd year. W. P. WYNNE.

HILDYARD JOHN EGLINTON DOBSON.

BORN FEBRUARY 18TH, 1902; DIED MARCH 28TH, 1927.

H. J. E. DOBSON, in whom is lost a young physical chemist of high promise, was born on February 18th, 1902, at St. Michael's Vicarage, Southfields, London, where his father, the late Rev. R. A. Dobson, M.A., was vicar for 25 years. His family had a definitely scientific connection, for his uncle, Major George E. Dobson, of Netley, was a Fellow of the Royal Society and was a personal friend of Charles Darwin and of Huxley.

After nine years at school at Monkton Combe, near Bath, Dobson entered University College, London, in 1919, as a student of science. During his undergraduate course he showed great promise in

chemistry, sharing the Tufnell Prize, a coveted distinction in these laboratories. His honours degree, of an unexpectedly low class, was no index to his merit; and this he showed at once by the success with which, aided by the Department of Scientific and Industrial Research, he proceeded to tackle research at University College on problems of solubility and activity in aqueous solutions. Papers which were an outcome of this work were published in the *Journal* in 1924 and 1925; and these afford the first accurate data for the partial pressures of water in hydrochloric acid, and of both water and alcohol in aqueous alcohol. He made many invaluable improvements in the technique of vapour-pressure work, of which that recorded in the *Journal* (1924, **125**, 1968) is only one instance.

In October, 1924, he joined, by invitation, the staff of the then new chemistry school at Durham, as lecturer in physical chemistry. Here, in spite of an illness which postponed his beginning duty, he set about his new work with great zest and success. At the same time he carried on energetically his studies of solution, both theoretically and practically; his originality of thought began to develop very markedly; and he has left a considerable volume of data and calculations which, if his health had allowed him to carry them a stage further, would undoubtedly have afforded a valuable contribution to physical chemistry.

Dobson's indomitable gaiety, gentleness, and enthusiasm, which he kept even during the long illness which proved fatal, won him affection from all his associates, both in the laboratories and in the college (Hatfield) of which he was a member at Durham. I. M.

ALBIN HALLER.*

BORN 1849; DIED 1925.

ALBIN HALLER, the eldest of a family of eleven, was born on March 7th, 1849, at Felleringen, a village in the valley of Thann-Saint-Amarin and not far from Mulhouse. From the village school he passed to the higher primary school at Wesserling, and the spectacle presented by the large factories of this busy industrial centre undoubtedly stimulated his imagination. He wished to become an engineer, but, at the age of fourteen, was apprenticed as a carpenter in his father's workshop. Two years later, however, as the result of a conversation with a pharmacist of Wesserling, he was brought into contact with his " bon génie," M. Achille Gault, and this event altered the whole course of his life. Haller loved to

* Based on Madame Ramart's Notice in the *Bulletin de la Société chimique de France*.

recall the period between 1865 and 1870, from the day when he walked over the hill separating his native valley from Mulhouse in order to present himself at the house of his first teacher to the time of his gaining the baccalauréat ès sciences. M. Gault was quick to appreciate the character and rare ability of his pupil; during three years the leisure which the direction of a laboratory allowed was devoted to Haller's scientific education and he then became assistant to M. Gault's brother, M. Léon Gault of Colmar, who instructed him in French and Latin.

The Franco-Prussian war supervened and Haller volunteered at Belfort, but in the sorrowful year 1871 he lost his father and, choosing to remain in France, had perforce to leave his mother and all that he remembered on the other side of the frontier. At Nancy he rejoined M. Gault, who had come to found a pharmacy and now continued to assist Haller in preparing for pharmaceutical examinations. Soon the University of Strasbourg was installed at Nancy and Haller became in succession aide-préparateur (1872), préparateur, and chef de travaux at the École Supérieure de Pharmacie. In 1879 he submitted his thesis for the doctorat ès sciences and from this time his advancement was rapid, so that in 1885 he became a professor in the Faculty of Science of the University. In 1899 he was called to the University of Paris and proved to be a worthy successor of Friedel and of Wurtz, adding fresh lustre to an illustrious record by his numerous researches, by his inspiring teaching and especially by his ability to communicate something of his own enthusiasm to his students. Haller was an able and energetic organiser; in relatively early days he was the prime mover in the creation of the Institut Chimique in the University of Nancy (1890) and, later, of that devoted to the study of physical chemistry and electrochemistry (1897). He was throughout his career actively interested in the co-operation of science and industry, and not least among his many services to his country must be reckoned the important part which he played in developing the teaching of applied science in France. In 1908 he succeeded Berthelot as President of the Commission on Explosives, and both civil and academic honours were showered on the ardent patriot and distinguished savant.

The scientific work of Albin Haller, extending over a period of fifty years, presents a striking example of the achievement that is possible when penetrating vision, amounting to intuition, goes hand in hand with remarkable powers of observation and sustained effort. It is impossible to give in a short space an adequate idea of the ground covered by Haller's original memoirs (of which there are nearly 250), but his researches in the camphor and phthalein

groups and on the elegant syntheses with the aid of sodamide must be briefly described or rather indicated. Subjects which cannot even be touched upon are, for example, Haller's work on pseudo-acids, on alcoholysis and on optical rotatory power.

The study of camphor and its derivatives was the object of Haller's earliest researches and he never completely abandoned the subject, since even in 1925 certain of his collaborators were engaged in this fascinating field of enquiry. We owe to Haller the demonstration that camphor is a ketone of the formula $C_8H_{14}<\begin{matrix}CH_2\\CO\end{matrix}$ and he also effected the final stages in its synthesis. Haller treated sodiocamphor with cyanogen chloride and thus obtained cyanocamphor, $C_8H_{14}<\begin{matrix}CH\cdot CN\\CO\end{matrix}$, which could be hydrolysed with formation either of camphorcarboxylic acid or of homocamphoric acid, $C_8H_{14}(CH_2\cdot CO_2H)(CO_2H)$, according to the experimental conditions. The familiar syntheses of the latter acid and of camphor from camphoric acid through camphoric anhydride and campholide are due to Haller. If we are to appraise these contributions to camphor chemistry at their true value it is necessary to recall that it was Haller himself who demonstrated that camphoric acid is a dicarboxylic acid; Friedel had suggested that it might be a keto-hydroxycarboxylic acid and Ostwald, from a study of the electrical conductivity of solutions of the acid, was led to concur in this opinion. The preparation of arylidene and alkylidene camphors by the action of aldehydes or ketones on sodiocamphor was of importance not only because it proved that camphor contains the group $\cdot CO\cdot CH_2\cdot$ but also because these substances were found to possess interesting optical properties and could be used as the points of departure in further syntheses.

Haller devoted much attention to clearing up the relations existing between the isomeric borneols, both natural and synthetic, characterising the former by the preparation of the related camphor, bromocamphor and camphoric acid. He concluded that the borneols and *iso*borneols are stereoisomerides to be represented by one and the same structural formula.

In order to avoid the partial reduction that occurs when sodium is employed in the preparation of sodiocamphor, Haller in 1904 investigated the action of sodamide on camphor and found that the products of a smooth reaction were sodiocamphor and ammonia. Sodamide had previously been used in organic chemistry for different purposes by some chemists, for example, by Titherley, Freund, and Speyer and by Brühl, but in Haller's hands it became a powerful auxiliary and new general synthetic methods were based on its use.

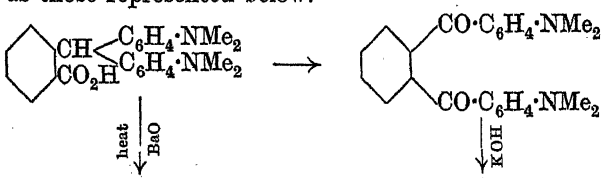
By its means the formation of the sodio-derivatives of ketones is a general reaction (acetone and acetophenone giving rise chiefly to condensation products) applicable to all substances of the forms $R{\cdot}CO{\cdot}CH_2R'$ and $R{\cdot}CO{\cdot}CHRR'$ and these sodio-derivatives may be brought into reaction with substances of various types. An important application is the progressive alkylation of ketones by means of sodamide and alkyl bromides or iodides through such stages as $R{\cdot}CH_2{\cdot}CO{\cdot}CH_2R$, $R{\cdot}CHR'{\cdot}CO{\cdot}CH_2R$, $CRR'_2{\cdot}CO{\cdot}CH_2R$, $CRR'_2{\cdot}CO{\cdot}CHRR'$, $CRR'_2{\cdot}CO{\cdot}CRR'_2$. The substances of the penta-alkylated acetone type are obtained by operating in ethereal solution and of them only pentamethylacetone reacts with hydroxylamine, semicarbazide and phenylhydrazine. The substances of the hexa-alkylated acetone type are obtained by operating in an aromatic hydrocarbon medium and do not condense with the above-mentioned reagents for the carbonyl group. On the other hand, these heavily substituted ketones may be readily and quantitatively reduced to secondary alcohols and, moreover, the ketones $Ph{\cdot}CO{\cdot}CR_3$, which are best prepared by Haller's method from the mono- or di-alkylated acetophenones, form with ease both oximes and semicarbazones. Haller made important applications of the method to the alkylation of cyclic ketones such as *cyclo*pentanone, *cyclo*hexanones, menthone, thujone, camphor, and indanone. He also employed such substances as trimethylene chlorobromide and thus obtained a series of δ-chloro-alkylated ketones. The polyalkylated ketones and their derivatives have naturally been of great service to students of molecular rearrangement and the theoretical interest of the study of their reactions and properties is inexhaustible.

Whilst carrying out experiments on the condensation of benzophenone and its derivatives with sodiocamphor (that is, camphor and sodamide) Haller noticed the formation of aromatic acids and amides. He was able to show that sodamide and benzophenone yield an additive product that is decomposed by water with the formation of benzamide, benzene, and sodium hydroxide. This decomposition was then found to be general for ketones of the form $R{\cdot}CO{\cdot}CR'R''R'''$, yielding either $R{\cdot}CO{\cdot}NH_2$ and $CHR'R''R'''$ or RH and $CR'R''R'''{\cdot}CO{\cdot}NH_2$ according to the nature of the substituents. A careful study was made of the circumstances governing the direction taken by the reaction and many interesting points emerged. Although there are exceptions, it was found to be a general rule that where the decomposition could yield an aromatic or an aliphatic acid amide, the latter course was favoured; *e.g.*, phenyl *tert.*-butyl ketone yielded benzene and pivalamide: $Ph{\cdot}CO{\cdot}CMe_3 + NH_3 \longrightarrow C_6H_6 + CMe_3{\cdot}CO{\cdot}NH_2$. Especially important in view of the use which Bouveault made of the method in con-

nexion with the chemistry of fenchone and camphorone is the extension of the study of this decomposition in the group of the cyclic ketones. Haller showed that fluorenone is changed by sodamide (and subsequent treatment with water) into *o*-phenylbenzamide. Similarly, 2 : 2′-dimethylindanone yields phenylpivalamide, which, like many of the products of these reactions, is difficult to obtain in other ways. As a third example, selected from many, the decomposition of dialkylated camphors by sodamide was found to yield the dialkylcampholamides.

Haller has also employed his method for the synthesis of certain pyrrolidines and tetrahydropyridine derivatives and in many other directions.

Whilst he was still at Nancy, Haller, in collaboration with Guyot, made some extremely interesting studies of certain phthalein, phthalophenone and anthracene derivatives. These were connected with the establishment of the constitutions of chemical individuals and with the mode of occurrence and mechanism of such transformations as those represented below.



leuco-Malachite-green. $C_6H_6+2NMe_2\cdot C_6H_4\cdot CO_2K$

Haller obtained the chloride of *o*-benzoylbenzoic acid in a crystalline condition and since it readily condensed with benzene in presence of aluminium chloride with formation of diphenylphthalide, he concluded that it should be formulated as phenylchlorophthalide. Another fruitful investigation was concerned with the preparation of *o*-(*p*-dialkylaminobenzoyl)benzoic acids and their conversion into the hitherto unknown dialkylaminoanthraquinones by successive reduction, cyclisation by condensation, and oxidation. Finally, by applying the Grignard reaction to anthraquinone, Haller made a long series of 9- and 10-arylated anthracenes and dihydroanthracenes.

The illness which proved so rapidly fatal was provoked by a laboratory accident and thus, at the age of seventy-six, Haller was carried away whilst still actively engaged in experimental work. He had expressed a wish that the end might come in this way.

Albin Haller was an inspiring and beloved teacher, a highly successful investigator of world-wide renown, and a great Frenchman, but he was also a man of fine character and as modest as he was distinguished.

R. Robinson.

RUDOLPH MESSEL.*

BORN JANUARY, 1848; DIED APRIL, 1920.

RUDOLPH MESSEL was the son of Simon Messel, a banker of Darmstadt. He was the second of five children, of whom four were to make their homes in England; the fifth acquired great distinction as an architect in Berlin. He lost his father when 11, and shortly after was sent to a Huguenot school at Friedrichsdorf in the Taunus, where he remained until he was 15 years old. His schoolmaster, Philip Reis, was the inventor of the first telephone. Messel, in his Presidential Address to the Society of Chemical Industry in New York in 1912, makes reference to the fact that he "assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit, speaking or singing, I listening at the other, or *vice versa*." About this time the family circumstances changed, and it was clear that Messel would have to become self-supporting at an early date. It was his intention to become an engineer, and in 1863 he discussed his further course of action with an old friend of his father's, H. Rau, then living in Frankfort. Rau appears to have advised Messel to devote himself to the study of commerce which he said would rapidly lead to independence, and to combine with this the study of Chemistry, Physics and Technology, and so become a manufacturer. It is clear that Messel's whole course of action was influenced by this letter, as not only did he keep it to the last among his rarest letters, but followed the advice it contained almost verbally.

In April, 1863, he became apprenticed to E. Lucius in his wholesale drug and chemical factory in Frankfort, and remained there until September, 1866, leaving to enter the Federal Polytechnic in Zurich, where he followed the regular first-year course. The following winter he spent at Heidelberg, studying physical chemistry under Erlenmeyer. He moved in the spring to Tübingen, where he finished his education, studying chemistry under Strecker, and continuing with him until April, 1870, carrying out work for which he obtained his degree. In April, 1870, he came to Manchester, originally to act as private assistant to Roscoe.

He was recalled to Germany owing to the outbreak of the Franco-Prussian war, where he served as a stretcher-bearer in the army of the Loire and was wounded. When recovered, he returned to England, where he remained during the rest of his life and ultimately became an Englishman.

He entered the service of Messrs. Dunn, Squire & Co., Stratford, as assistant to Dr. Squire. Shortly after, Squire formed with

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Spencer Chapman the firm of Squire, Chapman & Co., and took Messel with him in his new venture. This change occurred at a time when the growth of the synthetic dyestuff industry was threatened by the excessive price which was charged for fuming sulphuric acid, then produced by the old Nordhausen process in Bohemia. Squire decided to commence the manufacture of fuming acid.

In his New York Presidential Address, Messel tells of a conversation in the beginning of the '70's with his former teacher Strecker, and Brüning of Höchst, on the importance of fuming sulphuric acid in the synthetic alizarin industry. To his question how the acid should best be made, Strecker gave the reply: "That is a problem for you to solve." A few experiments convinced him, he says, that, given pure gases, the catalytic action of platinum was the rational solution of the problem. In April, 1875, a telegram came to him at the laboratory from Squire, asking him to read up that night about Nordhausen acid, as it was wanted by an Alizarin Works. The response was immediate and typical—no reading was necessary. Next day he showed how simple a matter it was to unite sulphur dioxide with oxygen by means of platinum. However, Squire was conventional and thought that the decomposition of acid sulphate would be a simpler method. Experiments were made, as requested, but eventually Messel was told to try his dodge.

Of the work that followed, no permanent record has been published, except in the form of Patents taken out by Squire in 1875. A year later, however, in April, 1876, Squire and Messel described and demonstrated the process before the Chemical Society. This paper was never printed, probably because of the Patent situation, but a paragraph in the "Chemical News" records the meeting. Messel treasured until his last days a document describing the experiments, and the original platinum apparatus used was left by him in his will to his lifelong friend, Professor H. E. Armstrong.

In his Presidential Address, Messel refers to the publication in October, 1875, by Winkler, of a process which was practically identical with his. Both investigators erred at that time in believing that stoichiometrical proportions of the gases were the best to use, and the various similarities gave rise to unpleasant comment. In letters to Messel, however, Winkler freely acknowledges the independence of Messel's work, and only regrets that he had deprived himself of the benefit of the invention by his publication.

The process was established at Silvertown, and in 1878 Messel succeeded Squire as manager of the works, which he only quitted in 1915, when his health gave way under the excessive strain of the times. The firm became Spencer, Chapman & Messel, Ltd., and the factory grew in size and importance.

Messel remained a bachelor and lived on the works. He was an indefatigable worker, and set a very high standard to all those who served under him. His sense of justice and sympathy, and the fact that he lived amongst them, gave him great popularity and power with his workpeople.

In the early days of the industry, the value of the fuming acid was much greater than that of oil of vitriol and the most suitable mixture of sulphur dioxide with oxygen was made by decomposing the latter. As experience was gained, and the difficulty of condensing the anhydride was overcome, sulphur dioxide prepared by burning sulphur and ordinary air were used, and later, excess of air was employed largely as a result of observation by the foreman that the plant worked better under these conditions.

It is a testimony to Messel's remarkable insight that right at the beginning he obtained such a wonderful knowledge of all details of this catalytic process, subsequently developed on a very large scale and in great detail by Dr. Knietsch and his co-workers of the Badische Anilin und Soda Fabrik.

Remarkable as Messel was as an industrialist, he was even more remarkable as a man. A man of astounding vigour and feeling, he had little thought for himself and a hatred of all display. He was essentially an artist, both in his extreme devotion to his own art of chemistry and in his love of the company of artists and other bohemians. He was everything—not only chemist, engineer and business man, but also took care to cultivate the social side of his life, and was almost the only manufacturer of his day who attended regularly at scientific gatherings and showed a real interest in the proceedings. His vigorous frame, black hair and sparkling eyes, his smiling face and peculiar guttural accent will remain in the memory of all who knew him. He never mastered English properly though he spoke it fluently. He was very fond of young people, many of whom rejoiced in his generosity. One of the most lovable of men, his outlook on life was always cheerful and optimistic. The example he set in leaving his fortune to science is a remarkable one and best proof of his considerate outlook. Honest and sincere himself, he hated insincerity and all meanness of spirit.

He played an active part in many scientific societies, particularly the Society of Chemical Industry, of which he was Foreign Secretary for many years and President for 1911–1912—probably the only connection in which he showed vanity, but he was very proud also of his election to the Royal Society in 1912.

His Presidential Address was written to show that science and industry are working hand in hand, and the importance of the results that such co-operation has produced. In discussing the

education of a chemist, he stressed the fact that too early concentration on special subjects had a bad effect on the development of the power and habit of thinking independently and on the faculty of imagination in the student. He held that technique is very rapidly acquired in practice by one who has been scientifically trained. With Carlyle he said, " He who has learned how to learn can learn anything," and the best system of education is the system which teaches each man how to educate himself. Gifted with his full share of enjoyment of the good things of this life, Messel nevertheless led a life of great simplicity. His success was due, in the first place, to his thorough scientific training and scientific outlook, but in an exceptional degree to his moral attitude towards his work.

He left four-fifths of his residuary estate to the [Royal] Society and the remainder to the Society of Chemical Industry. Without imposing any trust or obligation, he desired that the capital should be kept intact and the income applied to the furtherance of scientific research and other scientific objects. E. F. A.

IRA REMSEN.*

Two men, Ira Remsen and Wilhelm Ostwald, stand out during the last fifty years as great teachers and as founders of chemical journals which have had a profound influence on the development of chemistry. In these two respects their work is comparable with that of Liebig during the middle of the nineteenth century.

Ira Remsen was born in New York City, February 10th, 1846. His parents were both descended from the early Dutch settlers of New York and his mother had also Huguenot blood in her veins. For two years, from eight to ten, the boy lived in the country and had that intimate contact with nature which is impossible for a lad who spends his life exclusively in a city. A part of his early education was received in country schools. After further study in the public schools of New York City he entered the Free Academy, now the College of the City of New York, where he studied Latin, Greek, mathematics, history and a very little science. He did well in Latin and Greek and it was doubtless during those years that he laid the foundation for that perfect command of accurate English which has made it such a delight to read his books and to listen to his lectures. His interest in science seems to have been awakened at this period by the popular, illustrated lectures given by Dr. Doremus at the Cooper Institute.

He did not, however, complete the four years of work required

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for graduation at the Free Academy. Many years later he received the bachelor's degree from the College of the City of New York, as of the class of 1865. He was accustomed to say, with some pride, that he was one of the few men who had received the rank of M.D. from the College of Physicians and Surgeons without having received the bachelor's degree. He also said, at one time, that he thought he was the only university president in America who had not completed a four years' college course

After a few years in the Free Academy, Remsen's father decided that he should become a physician and apprenticed him to a doctor who taught in a homœopathic medical college. Here he read some chemistry and tried some chemical experiments for himself, sometimes with disastrous results to his fingers and clothing, as he told his students in recalling those days. He attracted the attention of his preceptor, however, and was made lecture assistant and quiz instructor in the college.

He soon revolted at the inefficient instruction and induced his father to send him to the College of Physicians and Surgeons of Columbia University. At the age of twenty-one he graduated and was supposed to be ready for the practice of medicine.

Once more he refused to be guided by the wishes of his father and, instead of entering a desirable partnership, which was offered him, with a well-known physician, he set out for Germany to study chemistry.

Liebig's name had attracted him to Munich and he had not learned that the great master had given up the direction of students some time before and had gone to the Bavarian University with the understanding that he could devote his time to his own studies and writing and that his duties should consist in giving a single course of lectures in inorganic chemistry. Remsen was forced to study with an able *Privatdocent*, Jacob Volhard. From him he received his first systematic laboratory instruction. Before that he had never performed the simplest analysis. Thorough training in analytical chemistry was, at that time, considered to be the only routine laboratory work necessary for the preparation of a chemist to begin research, and we may be sure that the fundamental basis for his career was well laid during this year of intimate association with Volhard.

During the summer of 1868, Wöhler made one of his friendly visits to Liebig and, through Volhard, Remsen was introduced to him and arranged to go to Göttingen in the fall. There he began research work under the direction of Fittig and two years later received his degree of Ph.D. at the age of twenty-four. When we remember that Remsen spent only one year in the systematic study

of chemistry and two years in research in earning his degree, we are tempted to question whether the long years of routine instruction which are required of young chemists to-day do not tend to dim that eager enthusiasm and repress the initiative so invaluable for a successful career.

It does not follow, however, that because Remsen did not take the varied courses of routine lectures which we expect of students to-day he failed to become very thoroughly acquainted with the chemistry of his times. He once told me that during his stay in Germany he read the volumes of Liebig's *Annalen*—150 volumes had been published in 1870—until he was acquainted with all the important papers published in that journal.

The same year that Remsen received his doctor's degree, Fittig was called to the professorship at Tübingen and he asked Remsen to go with him as his lecture and laboratory assistant. He continued in this position for two years and in this way, for five years in all, he drank in the spirit of the German laboratories.

It was a fortunate time for the eager, enthusiastic young man. In 1858 Cannizzaro had shown the importance of Avogadro's principle and laid the foundation for a system of true atomic weights. The same year, Couper and Kekulé extended Frankland's doctrine of valence to explain the structure of carbon compounds, and hundreds of professors and students were working together, after the model of Liebig's laboratory, in the fascinating world of organic chemistry.

It was at Tübingen, too, that a young Scotchman rang at the door one day and asked, in broken German, for the "Vorlesungszimmer." Remsen answered, "Oh! I guess you want the lecture room." So there was begun the life-long friendship with Sir William Ramsay. Only a few months before his death, Sir William wrote to Remsen, "Well, I am tired and must stop. I look back to my long friendship with you as a very happy episode in a very happy life; for my life has been a very happy one." When Remsen helped with the plans of the Kent Chemical Laboratory of the University of Chicago, he provided few rooms for isolated students and he made the remark that students learn more from each other than from their teachers. When two such students as Ramsay and Remsen met, we can well believe that this was true.

Remsen returned to America in 1872 and, after some delay, was appointed professor of chemistry and physics at Williams College. When he assumed his duties he found no laboratory and scant encouragement to teach science other than as a small element of general "culture" in an old-fashioned classical college. After a year, he was furnished a laboratory for his own use and there he

carried on researches on the action of ozone on carbon monoxide—a subject to which he returned some years later—and on *p*-sulphobenzoic acid. The latter led to an attempt to oxidise *o*-sulphobenzoic acid and its sulphamide and this, in turn, led to a long series of investigations carried out with students at the Johns Hopkins University. These studies finally established "Remsen's Law" that groups in the ortho-position interfere with the oxidation of alkyl groups of aromatic compounds by means of chromic or nitric acid.

As an illustration of the spirit of the New England colleges of that day, the following incident related by Professor J. M. Kingsley is illuminating:

"In the autumn of 1874, together with the rest of the junior class in Williams College, I began the study of chemistry under Professor Ira Remsen. After a few days I asked him for the privilege of carrying my studies farther in his private laboratory, as there was no laboratory work connected with the regular course. He replied to the effect that he would have to lay my request before the faculty, as there was no provision for such work in the curriculum. A few days later he asked me to stop after the class was dismissed, and then he informed me, in the most disgusted tones, that 'The Faculty, *in their wisdom*, have decided that you would break too much glassware and waste too many chemicals to allow you to work in my laboratory.'"

Kingsley became a zoologist of note instead of a chemist.

Shortly after his return to America, Remsen published a translation of Wöhler's "Organic Chemistry." He also published a beautifully written "Theoretical Chemistry." These books, and still more his persistence in research under discouraging conditions, attracted the attention of President Gilman, who was seeking men for his faculty at the Johns Hopkins University. He had already secured Gildersleeve for Greek, Rowland for physics and Sylvester for mathematics. Remsen was invited to Baltimore to meet the Board of Trustees and was entertained at a dinner at which he was seated beside one member of the board after another. In this way Professor Remsen became one of that galaxy who worked with President Gilman to organise the first genuine university in America, where more than half the students were graduates of other colleges and where the purpose was not so much to teach what is already known as to develop men into productive scholars and add to the world's knowledge. President Gilman had the somewhat rare quality of fully trusting the men he selected and allowing them to develop the work of their departments without interference. His injunction to Remsen was, "Do your best work in your own way."

Professor Remsen followed rather closely the models with which

he had become so familiar in Germany. He gave lectures on inorganic chemistry during the first semester and on organic chemistry, the second. These were well illustrated with experiments and he had a crystal-clear, masterful method of presenting his subject. Once a week there was a meeting of graduate students for reports on current literature.

But the most important and vital part of his instruction was the daily visit to the desk of each research student. Often, at critical points, he would stop and work for minutes or for an hour or more with the student, and the product, in the end, was the joint work of professor and student, as it had been in Liebig's laboratory. Most of the topics studied grew, directly or indirectly, from his investigation of the oxidation of *p*- and *o*-sulphobenzoic acids and the law of the protection of ortho-alkyl groups from oxidation.

Quite early in the course of these studies, Fahlberg, working under his direction, discovered that the *o*-sulphamide of benzoic acid may be easily oxidised by potassium permanganate in a neutral or faintly alkaline solution. The product was called by Remsen benzoicsulphinide. It is several hundred times as sweet as sugar and some years later Fahlberg developed the commercial production of the compound under the name of saccharin.

The discovery of benzoicsulphinide naturally led to the investigation of many other similar compounds. This also led, rather directly, to the discovery of the sulphonephthaleins and the study of the chlorides of sulphobenzoic acid. Professor Reid reports how he came to study the decomposition of diazonium compounds with alcohol. The laboratory book said "add alcohol and smell the aldehyde." A student came to him and said he did not smell aldehyde. Remsen took the tube and could not smell aldehyde either. He made this into a good story, telling how stubborn the student was who wouldn't smell aldehyde when told to do so.

The work of Professor Remsen and his students never degenerated into the mere preparation of new compounds. He always endeavoured to establish some general principle in relation to the substances prepared.

In 1883 Professor Remsen came back to the action of ozone on carbon monoxide and a very careful investigation demonstrated that the latter is not oxidised when the mixture with ozone is heated to 300° and the ozone is completely decomposed. He also, in an investigation which proved that phosphorus usually contains a little carbon, demonstrated that carbon monoxide is not oxidised when mixed with air and passed over moist phosphorus, although ozone is formed in quantities. A satisfactory theoretical explanation of these remarkable results is still to be found.

In 1889 Professor Remsen made an exhaustive study of the literature of the double halides and found that, with very few exceptions, the number of molecules of an alkali halide combined with one molecule of another halide is equal to or less than the number of atoms of chlorine in the other halide. A considerable number of experimental investigations were carried out with his students to test the validity of this generalisation. The conclusion that two chlorine atoms unite to form a bivalent group has not been generally accepted and does not agree well with the more recent electronic theories of chemical combination.

When Remsen went to Johns Hopkins University in 1876, there was no satisfactory medium in America for the publication of an account of his researches. A few of his articles were published in *The American Journal of Science*, but Professor Dana, the editor of that journal, soon decided that researches in organic chemistry did not furnish material of sufficient interest to his readers and advised publication abroad. Professor Remsen was not satisfied with this and, with the aid of other chemists, he established *The American Chemical Journal*. With far-sighted vision, he made this a medium of publication for American chemists and not an organ of the Johns Hopkins University. For thirty-five years this journal was a very important agency for the promotion of genuine chemical work. It was the first American journal in this field which secured widespread recognition abroad and it would be difficult to overestimate its value in stimulating chemical work and in placing Americans in their rightful place among the chemists of the world. At the close of the fiftieth volume President Remsen decided that publication in America would be better served by incorporation of *The American Chemical Journal* with *The Journal of the American Chemical Society*. This was done and the latter journal carries on its title page a record of the consolidation of the two journals.

Remsen's first book was a " Theoretical Chemistry," written while he was at Williams College. It passed through five editions and was translated into German and Russian. His " Organic Chemistry " was published in 1883 and has been the medium through which many chemists, physicians and others have been introduced to the subject. His text-books of " Inorganic Chemistry," both elementary and advanced, are characterised by a logical, lucid style which has made them very popular and widely used. The " Organic Chemistry " was translated into many foreign languages and several of the other books were also translated.

A long series of students, trained in intimate association with Professor Remsen, are now widely scattered and many of them hold important positions as teachers and in the industries. They

look back to him as to a father, who always required high quality in their work, who was wise in his advice and helpful in their difficulties.

Professor E. E. Reid writes, " It is impossible to characterise or describe Remsen. He had a keen sense of humour and a ready wit, a personality in the fullest sense of that term. He drew people to him but always kept them in their place."

In 1881 Boston had trouble with her water supply and Professor Remsen was called upon for his advice. He was fortunate enough to discover the cause of the difficulty. On many other occasions he was called upon for public services to Baltimore, Maryland, and the United States. He was for some years a member of the Good Roads Commission of the state.

In 1901 Remsen succeeded D. C. Gilman as president of Johns Hopkins University. The resources of the university had been depleted by the depreciation of some of its securities and the period of his administration was a difficult one. In spite of this, the university continued its steady and satisfactory development. The school of engineering was founded and the cramped quarters in the heart of the city were exchanged for the magnificent campus which the university now occupies in the outskirts of Baltimore.

President Remsen retired in 1913. After that he spent his time in travel, in revising his books, in work for the Government as chairman of the Referee Board organised during Roosevelt's administration to consider questions pertaining to the law for the control of food products and their adulteration, and in consulting work for one of our largest industrial corporations. He died at Carmel, California, in 1927, at the age of eighty-one.

He was the recipient of many honours. The degree of LL.D. was conferred by Columbia, Princeton, Yale, Toronto, Harvard and Pennsylvania. He was a foreign fellow of the London Chemical Society and foreign member of the French Chemical Society. In 1902 he was president of the American Chemical Society; in 1903, of the American Association for the Advancement of Science. During 1907—13 he was president of the National Academy of Sciences. In 1908 he was awarded the gold medal of the Society for Chemical Industry and in 1910 was president of that society. In 1914 he received the Willard Gibbs medal of the Chicago Section of the American Chemical Society.

In his boyhood Remsen was reared in a very strict, religious atmosphere and he retained a simple religious faith throughout his life. In his address " On the Life History of a Doctrine," delivered as president of the American Chemical Society, after pointing out that " faith is called for at every turn in scientific matters as well as spiritual," he said, " It would be as illogical to give them (atoms)

up as it is, in my opinion, to deny the existence of a power in the universe infinitely greater than any of the manifestations familiar to us; infinitely greater than man; a power that 'passeth all understanding.'"

WILLIAM A. NOYES.

EDWARD HENRY RENNIE.

BORN 1853; DIED JANUARY, 1927.

THE intellectual life of Australia suffered a heavy loss early last January, when Dr. Edward H. Rennie, Angus Professor of Chemistry in the University of Adelaide since 1885, died suddenly from heart failure at the age of seventy-four. Though he had long earned retirement, he remained in active work to the last, devoted, as always, to the promotion of education and of science in Australia.

His affection for that sunny land was native—not acquired, as it has been by so many of those engaged in University work there; for he was born and educated in Sydney, where his father, E. A. Rennie, was Auditor-General of New South Wales. His urge towards an academic life is, no doubt, to be traced back to his grandfather, James Rennie, who was Professor of Zoology at King's College, London, nearly a century ago. After graduating in Arts at the University of Sydney, he spent a few years as a school teacher there and in Brisbane; but in 1877 he went to London, bent on pursuing the study of chemistry. Before returning to Australia in 1882, he had obtained the London D.Sc. and had published a number of papers in the *Journal* of the Chemical Society. Some of these were on work done conjointly with Alder Wright, whose assistant he was for a time at St. Mary's Hospital Medical School. He came also under the influence of Professor H. E. Armstrong (the stimulating effect of which so many young chemists then and later could testify to), and the friendship thus formed lasted through his life, maintained by correspondence and revivified in 1914, when the British Association visited Australia.

Apart from certain investigations with Alder Wright in chemical dynamics (a subject then in a somewhat embryonic state), Rennie's researches at this time were organic and for the most part dealt with the chemistry of various Australian plants. His special interest in this field was to remain with him always. During the first ten years of his tenure of the Adelaide chair he contributed to the Society's *Transactions* seven papers on various Australian plant products; but thereafter he had but little leisure from teaching and administrative duties, and some of it was given to inorganic and

physical work. More recently, however, he took up the investigation of the resins of *Xanthorrhœa*, a peculiar and characteristic Australian plant.

As a teacher, Rennie was exceptionally conscientious and thorough. He had but little assistance, for it is only of late that the Australian Universities have been able to indulge in elaboration of staff (still very incomplete), and he found it necessary personally to teach chemistry in all its branches, organic, inorganic, physical, and analytical. The writer, who saw as much of him as was compatible with residence five hundred miles apart, can testify to his zeal in keeping abreast of modern advances, even in fields that did not specially appeal to him.

As a member of his faculty and of the governing council, frequently as acting Vice-Chancellor, and as chairman of the affiliated School of Mines, he did invaluable work for his University. In wider fields too his wise judgment, experience, and authority were of service to the country. He was the chairman of the South Australian branch of the Commonwealth Council of Science and Industry. In the last year of his life—perhaps the busiest—he was President of the Australian Chemical Institute and also President of the Australasian Association for the Advancement of Science; and his address at the Perth meeting of the Association included a valuable survey of Australian plant chemistry, past, present, and future.

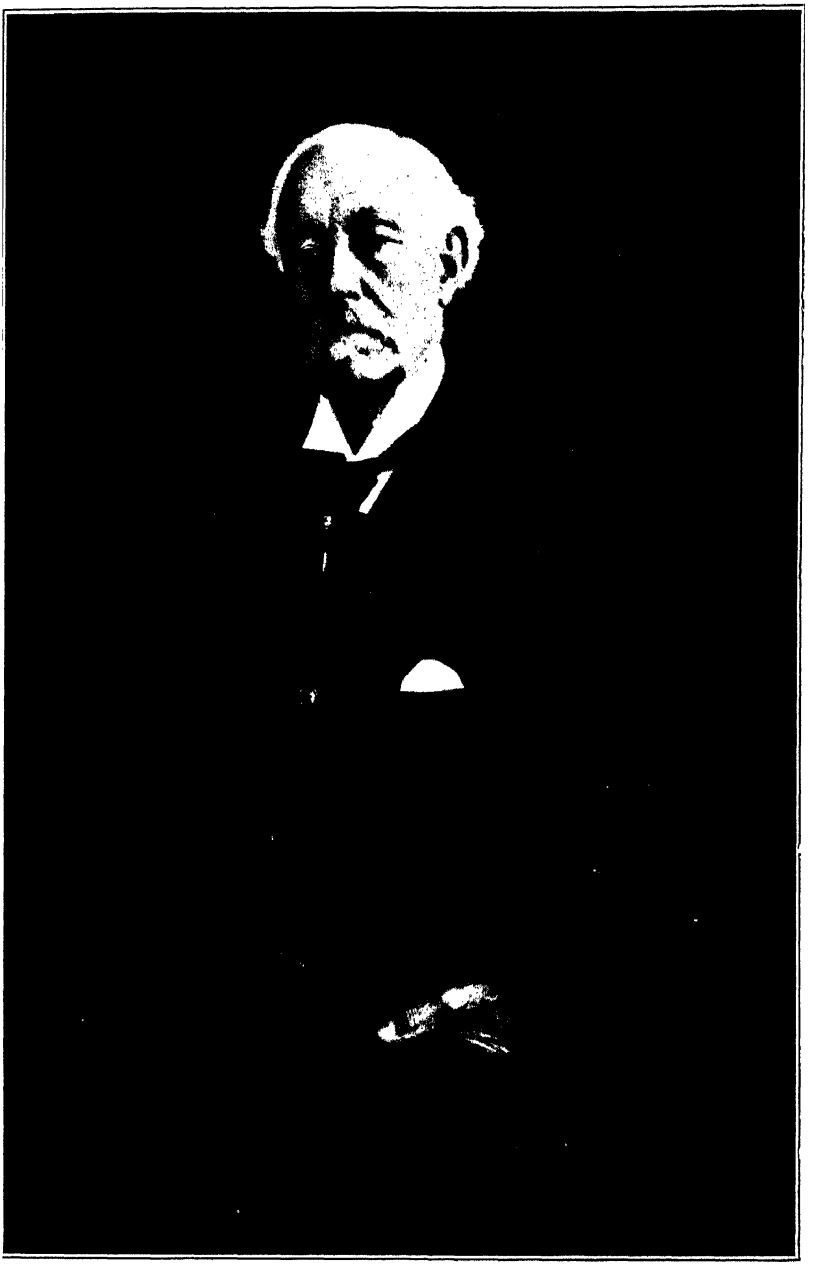
As a man, Rennie was of simple tastes and rather austere habit of life, and there was an orthodox side to him best known to his fellow elders of the Chalmers Church in Adelaide. But his warmth of heart and human sympathy endeared him also to others. And the writer is among these; for Rennie, then a stranger, was the first to welcome him on Australian soil in 1886, and forty years of friendship followed.

D. O. M.

SIR WILLIAM AUGUSTUS TILDEN.

BORN AUGUST 15TH, 1842: DIED DECEMBER 11TH, 1926.

HASTED'S History of Kent states that John Tilden purchased Ifield Court, Northfleet, in 1766; the grandson of John Tilden was Augustus and had two sons, the elder being William Augustus, born in the parish of St. Pancras on August 15th, 1842. The brothers were unfortunate in their schooling. In 1845 their father had exchanged a clerkship in the Bank of England for the managership of the Kidderminster bank, but retiring from this post in 1852 he remained without business occupation until his death at Bedford



SIR WILLIAM AUGUSTUS TILDEN.

[*To face p.* 3190.]



in 1879; it thus happened that the boys were never kept for long at any one school. Their mother, however, was a woman of strong character and marked ability, devoting herself unreservedly to the care and instruction of her children during their early home-life; this benefit was uniformly recognised with affection by her sons, and having passed her concluding ten years in the household of William Augustus, she died in 1900 at the age of 94.

When eight years old the boy was placed as a boarder with Rev. Edward Brine, second master at Kidderminster Grammar School, remaining only two years because the family moved to Bedford. Here he was entered at the Commercial School, now called the Modern School, but after three years was transferred for one year to the charge of Mr. George Vasey, who limited his pupils to five, imposed upon them a vegetarian diet, and taught them the rudiments of anatomy, physiology, botany, zoology, mechanics and optics illustrated by diagrams which the lads were required to copy. Another break occurred in April, 1856. The boys' maternal grandfather, Mr. Henry Balls of Cambridge, had now undertaken responsibility for their education and he sent them to East Dereham, where Rev. Joseph Thompson kept a school of about 70; here William Augustus received his first contact with chemistry, and the demonstrations of a visiting master from Norwich inspired him with a desire to experiment on his own account.

Animated by the vague ambition to become a chemist, young Tilden was almost inevitably projected into pharmacy. His friends of that period would naturally reach a conclusion which remains, even after seventy years, a widespread popular superstition; and although the College of Chemistry was already operative under the direction of Hofmann, they cannot be blamed for what would then appear to be the normal procedure. So, in August, 1857, the lad was apprenticed for five years to a pharmacist of Barnsbury, Mr. Alfred Allchin.

This association was propitious, for Mr. Allchin took a liberal view of the relation between master and apprentice. He had been laboratory assistant at the Pharmaceutical Society, had worked for a short period in Paris with Pelouze and had joined the Chemical Society. Appreciating these advantages, he encouraged young Tilden to attend the Pharmaceutical Society's lectures on chemistry, pharmacy, botany and materia medica, permitting him to spend the whole of his fifth year in the laboratory of the School. Allchin's generosity was not limited to these benefits. He entered his apprentice for Hofmann's course of lectures at the Royal College of Chemistry, and this period was a critical one in the history of chemistry; for students were perplexed by the novel notation and

modified atomic weights introduced by Gerhardt and Cannizzaro. Hofmann's lectures were Tilden's compass, and in October, 1861, the young pharmacist gained the first Bell scholarship.

Another favourable influence on young Tilden was the friendship of Dr. John Stenhouse. Ill-health had led Stenhouse to relinquish his lecturership at St. Bartholomew's Hospital and equip a laboratory in Rodney Street, Pentonville, whence issued the series of investigations into natural products distinguishing the joint authorship of Stenhouse and Groves. Stenhouse frequently visited Allchin's pharmacy, greatly to the encouragement of young Tilden, whose preparative work he often commended, and whom he subsequently admitted to his laboratory as a junior assistant on sixty pounds a year. In 1863 Tilden became demonstrator at the Pharmaceutical Society under Attfield, who was then professor of practical chemistry while Redwood continued to give the lectures; and here he remained until 1872.

These nine laborious years encircled the transformation of a pharmacist into the chemist. In this development the London University system of graduation played an important part. Although no "cobbler from Cornwall," Tilden was one of an abundant upward-struggling community to whom the prospect of a definite academic hall-mark offers an elevating incentive to self-improvement. He toiled at French, German, Greek and Latin for matriculation, and in 1868 graduated B.Sc. with honours at an age which disqualified him from gaining the university scholarship. This was followed in 1871 by the D.Sc., in those days attainable by examination only; Tilden's examiners were Debus and Odling. Meanwhile, in the scanty leisure snatched from these pressing demands, he began publishing papers in the Journal of the Chemical Society, his first contribution (1865) dealing with periodides of organic bases.

A new chapter opened in 1872, when Tilden was appointed senior science-master at Clifton College, under the headship of Dr. John Percival, afterwards Bishop of Hereford. At that date the school was ten years old, and was directed by a remarkable man. Percival had proceeded from Rugby to Oxford (1854—58) and there took firsts in classics, mathematics, and physics; he aimed at moulding Clifton as an all-round school, a breakaway from the purely classical tradition, and his first group of assistants included A. Leipner, afterwards professor of botany at University College, Bristol. Later teachers of chemistry and physics were A. W. Reinold, John Perry, Tilden, and Shenstone, the first laboratories being opened in 1866 and followed by those for biology and zoology in 1869. The standard of effort appears to have been high. Laboratory classes, lecture courses and private coaching could not have left much time

for his own experiments, but somehow Tilden found it, and found also a valuable collaborator in W. A. Shenstone. The partnership was happy for both. Tilden had married before leaving London, and Shenstone was one of the household during the two years preceding his transference to Taunton in 1875. A joint paper on aqua regia and the nitrosyl chlorides appeared in that year, and work there described was the progenitor of pinene nitrosochloride. With exacting enthusiasm, for he was not physically strong, Shenstone went over to Clifton for the long vacation following his transfer, and the friends occupied their holiday in rectifying such essential oils as were then available, separating the terpenoid components and converting these into nitrosochlorides by the new agency. The results were published in 1877, and came to be recognised as a turning-point in the path of terpene chemists, leading to a fresh view of the hydrocarbons themselves and providing a trustworthy means of identification.

Meanwhile, an important municipal development had proceeded in Birmingham. Sir Josiah Mason (1795—1881), having amassed a fortune from humble beginnings, had the noble ambition to provide for others the educational opportunities denied to himself, and allocated £180,000 to the foundation of Mason College. The new institution was opened in 1880 and Tilden was appointed the first professor of chemistry in association with J. H. Poynting (physics), M. J. M. Hill (mathematics), and T. W. Bridge (biology). It may be readily imagined that the task of building up the organisation and tradition of Mason College would evoke physical and mental resources of a high order, and the success with which this early work was accomplished is reflected in the great midland university at Edgbaston representing the modern response of Birmingham to its largely augmented educational demands. The part which Tilden played in this constructive labour merits the fullest possible recognition. In addition to high professional competence early marked by election to the Royal Society (1880), he was endowed with a social quality which is unhappily rare. It has been said that the really well bred man is he who can enter —and leave—any mixed company of people to whom he is unknown without necessarily revealing his occupation in life. The searching requirements of such a specification were engagingly met by Tilden, whose conversation and appearance would have puzzled a casual acquaintance to decide whether he was an army officer, Indian civil servant, artist, metropolitan magistrate, man of leisure, or even an ambassador.

Adaptability so wide and graceful was particularly valuable in a society of the complexity comprised in Birmingham of the eighties. To harmonise aspirations of prosperous young amateurs with more

serious ambitions of the needier students; simultaneously to convince the Birmingham citizens that a man of science is not necessarily an eccentric anchorite, but that in belonging to their own world he might add to its attractions; withal to develop an ever-widening grasp of a rapidly growing science, were tasks which few chemists of his generation could have accomplished so successfully. At the beginning of his tenure, moreover, Tilden found that provision for instruction in metallurgy had not been made, and being without practical knowledge of the blast-furnace and steel manufacture, he became indebted to several of the large ironmasters, including Mr. Robert Heath, then M.P. for North Staffordshire, and Sir Isaac Lowthian Bell for the privilege of admission to their works. Soon afterwards, however, this branch of the curriculum was entrusted to Mr. Thomas Turner, who subsequently became the professor of metallurgy. In spite of these demands, Tilden continued the research on terpenes which had begun so auspiciously at Clifton. The first completed work dealt with decomposition of the hydrocarbon vapours by heat, and it was during a study of isoprene produced in this manner that its transformation into caoutchouc was discovered. Thus, both scientifically and socially, Tilden's life in Birmingham was a full and active one. He occupied a pleasant house in Harborne Road, took interest in his garden and continued to enjoy lawn-tennis until well past his fiftieth year. This may not appear unusual to a generation witnessing that indefinite extension of youthful activities engendered by golf, automobiles and jazz-discords; but post-war youth, rivalled in its thirst for amusement by a crowd of age-defying seniors, cannot be expected to realise that in those days men were "too old at forty," while coeval women wore caps.

Tilden's life was now widening its boundaries, for his reassociation with London grew considerably during the last few years of his Birmingham connection. He had executed several examinerships, including that in chemistry for the Science and Art Department; he sat in the council of the Royal Society (1892—4), and a continuous adherence to the Institute of Chemistry had culminated in his election to the presidency (1891—4). This office in particular made heavy calls on Tilden's time and attention, for the period was a critical one in the history of the Institute. Much controversy centred in the question of admission and the type of training which might most appropriately lead thereto. Several conferences took place; regulations were finally accepted in October, 1893, and remained the basis of those controlling admission during the twenty years following. The two main requirements were (1) three years of systematic training in chemistry, physics, elementary mathematics

and an optional other branch of science, associated with (2) three examinations, preliminary, intermediate (in general theoretical and practical inorganic and organic chemistry), leading to the final, in a branch of chemistry elected by the candidate from a prescribed list. Concurrently with this consolidation, an important geographical change occurred. Since 1884, the Institute had been a tenant of the Royal Statistical Society at 9, Adelphi Terrace, depending on the hospitality of the various London laboratories for examination facilities. At the beginning of 1893, however, the Institute moved to 30, Bloomsbury Square, thus for the first time enjoying dignified and ample premises of its own. Having acquired the remaining twenty-two years of lease, it seemed justifiable to build and equip the laboratories necessary for conducting practical examinations, and they were formally opened by the president on December 8th, 1893. In the same year the bye-laws were revised, and authority was given to an important definition by the censors concerning professional conduct; a seal was designed, incorporating the figure of Priestley as represented in Williamson's statue viewed from the old Mason College windows.

In the autumn of 1894, Tilden succeeded T. E. Thorpe as professor of chemistry in the Royal College of Science, London, and was destined to remain at South Kensington until 1909, when Sir Edward Thorpe returned for three years on retirement from the Government Laboratory. The period of Tilden's occupancy was important in the college history, covering the transference of the chemistry department from the conspicuous red building on the eastern side of Exhibition Road to its present domicile. Moreover, the change was concurrent with a modification in status effected by incorporating the Royal College of Science and the Royal School of Mines with the Central Technical College of the City and Guilds of London Institute: this occurred in 1907, when the two royal colleges were detached from the Education Department and united with the Guilds' Engineering College to form the Imperial College of Science and Technology. In prospect and achievement this transformation threw much extra work on Tilden and his physics colleague, A. W. Rücker, the consequent interruption to their systematic duties beginning about 1899, when Sir Aston Webb was commissioned to prepare the plans.

These last fifteen years of Tilden's professorial career were crowded ones. Interwoven with his college duties were the periodical demands of the Board of Education examinations and the continuous attention he gave to the Chemical Society. The Royal Society, which he served as a Vice-President during 1904—6 was another time-absorbing interest, and for a brief term he joined the Senate of

London University, having been elected a Fellow in 1899. Although these various legitimate distractions inevitably diminished the time given to research, he nevertheless maintained an interest in the field which had brought him fame, and broke new ground by a systematic study of specific heat; this work was continued for several years, and the earlier results were assembled in the Bakerian Lecture to the Royal Society for 1900. It was not surprising that about the time he was due by age to retire, Tilden incurred a slight breakdown in health; his friends had sometimes wondered at the unfailing regularity with which he had fulfilled his duties, because he did not give an impression of robust physical condition at any period of his later life. In view of the difficulty found in replacing him, however, Tilden was persuaded to remain until a suitable successor (Sir Edward Thorpe) could be found, and this arrangement was facilitated by delegating the lectures to his trusted colleague, Dr. G. T. Morgan.

Liberation from official duties in 1909 was accompanied by the distinction of knighthood and the title of Emeritus Professor, but only changed the form of Tilden's mental activity. He had intended to continue the experimental work which had been so much interrupted in later years, and for this purpose retained the use of a laboratory at the Imperial College; but his physical condition precluded sustained bench-work, and the project was necessarily abandoned. His retirement to the home he had already made at Northwood was therefore devoted to literary pursuits which took shape in four books, "The Elements" (1910), "Chemical Discovery and Invention in the Twentieth Century" (1917), "Life of Sir William Ramsay" (1918), and "Famous Chemists" (1921).

These volumes represent a substantial achievement indeed for the eighth decade of any man's life, and bear testimony to the unabated ardour with which he assembled and imparted knowledge. They involved frequent and sustained consultations in the Burlington House libraries, and scarcely diminished the regularity of his attendance at scientific meetings. In fact, it may be stated here that among the many claims of Sir William Tilden's life to the respect and admiration of younger chemists was the devotion he showed to the Chemical Society by his constant attendance at its meetings. He became a Fellow on June 1st, 1865, joining the Council as an ordinary member thirteen years later. Thereafter, in one capacity or another, he served as councillor thirty-seven years, comprising twenty-eight as Vice-President and four as Treasurer (1899—1903), occupying the presidential chair in the period 1903—5; his last appearance in Burlington House—and he seemed to know it would be the last—was on March 27th, 1924, when he

spoke to a resolution at the annual general meeting. Thus, in various ways and always disinterestedly, he well and truly served the body which assembled most intimately his professional friends and their joint scientific interests. The Annual Reports on the Progress of Chemistry, inaugurated in 1905, will remain a lasting memorial to this loyal devotion, being the concrete feature of his presidency.

Before the foundation of the Imperial College, Tilden was appointed Dean of the Royal College of Science and the Royal School of Mines. He was awarded the Davy Medal (1908), received honorary degrees from the Victoria University, from Dublin and from Birmingham, and was elected a member of the Athenæum under Rule II (1907). In 1869 he married Miss Charlotte Pither Bush of St. Heliers, Jersey, who died in 1905 leaving one son, Mr. Philip Armstrong Tilden, the architect. His second marriage took place in 1907, Lady Tilden having been Miss Julia Mary Ramié, also of St. Heliers, and in the knowledge that his twilight years were happy, peaceful and well-ordered his friends too have been happy. His death occurred on December 11th, 1926.

Tilden's active participation in chemical research continued throughout a period of more than forty years, during the earlier part of which, as might have been expected from the contemporary chemical atmosphere and his association with pharmacy, his experiments dealt with natural products. Thus his first paper (1865) described periodides of caffeine, strychnine and brucine, and his next inquiry (1872) related to the crystalline substances obtainable from aloes, to which he returned several times (1875 and 1877); comparison was made between Barbadoes, Natal, Socotrine, and Zanzibar aloes, from which a derivative of methylanthracene, oxygenated to the composition $C_{15}H_{10}O_6$, was obtained with chromic acid. An early paper displaying keen chemical insight and skilful technique was that on aqua regia and nitrosyl chloride (1874), showing how the latter substance may be obtained as an individual and proving the composition of its molecule to be NOCl; at the same time, it was established that the supposed nitrosyl dichloride and dinitrosyl sulphate of Gay-Lussac were actually fortuitous mixtures.

It was a natural consequence that the new agent should be applied to organic substances, and a beginning was made with phenol (1874) which gave chloranil, followed by turpentine (1875) giving the subsequently famous nitrosochloride of pinene, from which "nitrosoterpene" was prepared by the action of alcoholic sodium hydroxide. It was at this period that Shenstone had joined Tilden, and the two young men were quick in recognising that the confusion prevailing in essential oil chemistry might be dispersed by the new weapon;

but it is evident from the title of their paper, "Isomeric Nitrosoterpenes" (1877) and the procedure therein described, that at this stage of the inquiry they expected the nitrosochlorides to be less important means of identification than the nitroso-derivatives obtainable from them by removing the elements of hydrogen chloride. Thus the nitroso-derivative made from turpentine (American and French), oil of sage and oil of juniper was found to be identical in each case, and was distinct from that formed when the nitrosochloride of hesperidine, caraway, and bergamot oils is heated. The authors, however, already believed that "the result of the further application of this method will be to show that a great many of the natural terpenes are merely physical isomerides not differing from one another in chemical constitution."

During the two following years (1878—9) the terpene-alcohol terpineol was characterised. Earlier workers (Wiggers, List, and Oppenheim) had found that dilute acids convert the crystalline terpene hydrate into an oil which they called terpinol and believed to have the composition $C_{20}H_{34}O$. Tilden's investigation showed the oily product to consist principally of terpineol, $C_{10}H_{17}\cdot OH$, associated with a hydrocarbon, $C_{10}H_{16}$, afterwards identified with dipentene. At the same period he studied the hydrocarbons of Russian turpentine oil, and published the views he had been led to form regarding the constitution of camphor and the terpenes.

After an interval of about five years there appeared his well-known paper "On the Decomposition of Terpenes by Heat" (1884). The process therein described is a fore-runner of the modern operation of "cracking" petroleum, and allowing for difference in the starting-materials, the products of the two changes correspond. It was found that when the vapour of turpentine oil is passed through a heated iron tube on which redness is just visible in darkness, gaseous and condensable hydrocarbons are produced in great variety. Dipentene, *p*-cymene and colophene, with smaller proportions of benzene, toluene and *m*-xylene were isolated, but the most important and interesting product was the volatile hydrocarbon, isoprene, C_5H_8, obtainable also by the dry distillation of caoutchouc. In this connexion it may be claimed that the earliest production of synthetic rubber was in the hands of Tilden (1892), because a few years after the foregoing investigation he noticed that in a closely sealed bottle containing a specimen of purified isoprene there had appeared a sticky product which, when withdrawn and manipulated, showed those properties of rubber subsequently associated with sodium-polymerised isoprene. Although aware of what had occurred, and displaying this rubber as an object of interest to his friends, Tilden did not standardise the conditions of transformation, and it is not

difficult to reconstruct his probable attitude of mind by remembering that automobiles were not even threatening to arrive, and that the "synthesis" was virtually a passage from one tree-juice to another by de-polymerisation *cum* re-polymerisation. Moreover, in spite of all the attention directed to this matter in the pregnant thirty-five years intervening, the exact conditions of transformation remain obscure.

Tilden reviewed at some length the confused ideas then (1888) current on the constitution of terpenes and later (1893) showed that dipentene does not give toluic acid on oxidation; he proved that the hydrocarbon recovered from dipentene dihydrochloride must be a mixture, because it yields over 27 per cent. of toluic acid. In the next few years (1893—1895) he resumed attention to nitrosyl chloride, preparing phenylazoimide by its action on phenylhydrazine in acetic acid and incidentally discovering an alternative method of preparing hydrazoic acid by hydrolysing *p*-nitrophenylazoimide. These experiments embraced a very wide range of typical unsaturated compounds in a study of nitrosyl chloride with reference to its additive capacity. Its action on amides was then surveyed, and while oxamide, oxanilide, succinimide, and phthalimide were indifferent, other amides were found to undergo loss of nitrogen and, in the case of asparagine and aspartic acid, chlorination; lævo-rotatory asparagine gave lævo-rotatory chlorosuccinic accompanied by fumaric acid.

About 1890, Tilden had received from the West Indies a butterlike solid occurring as a by-product in the manufacture of Montserrat lime-juice. Isolation and characterisation of limettin, so named from *Citrus limetta*, gave much trouble, and the investigation remained unfinished in Birmingham; but later (1902) he was able to show that limettin is 4 : 6-dimethoxycoumarin, $C_{11}H_{10}O_4$, giving phloroglucinol with concentrated potash, and undergoing chlorination, bromination, and nitration.

The concluding papers dealt with carbon compounds all related to the nitrosochlorides of pinene and limonene, thus providing a seemly epitaph to Tilden's early chemical interest. By the simple device of using an inactive mixture of American and French turpentine in place of an optical individual, the yield of nitrosochloride was greatly improved (1904), and was brought to the 55 per cent. obtainable from the inactive pinene produced when methylaniline or dimethylaniline acts on the nitrosochloride. This, and the two nitrosochlorides of limonene, were then found to exchange their chlorine atom for the cyano-group when heated with alcoholic potassium cyanide (1904—5), the products being unimolecular: the compound thus obtainable from limonene β-nitrosochloride was

identified with cyanodihydrocarvoxime. The corresponding pinene derivative is also a cyano-oxime, and undergoes hydrolysis in successive stages to an aminodicarboxylic acid which remained (1906) unidentified. A curious difference between pinene and limonene nitrosochlorides in action with magnesium methyl iodide revealed itself (1905—6), for while the bimolecular pinene nitrosochloride yields two unimolecular compounds (1905), in one of which the chlorine atom survives, the two products from limonene nitrosochlorides (1906) are still bimolecular and isomeric, having lost one atomic proportion of oxygen. At the same time it was found that the process of reducing nitrosopinene to pinylamine may be carried to the further stage of dihydropinylamine, identical with the base arising from the oxime of pinocamphone on reduction (1906).

The second main division of Tilden's researches has been summarised in contributions to the Philosophical Transactions of the Royal Society, and arose from the conflict of opinion regarding the atomic weights of nickel and cobalt; it deals with the specific heat of metals, and the relation of specific heat to atomic weight. Tilden's original purpose, conceived about 1895, developed into the wider field of testing further the law of Dulong and Petit, and the opening experiments on cobalt and nickel were subsequently extended to gold, platinum, copper, iron, silver and aluminium. Great care was exercised in purifying the metals initially used, and a long series of experiments with them was made in the Joly differential steam-calorimeter. As the inquiry widened, however, the range of temperature was extended through that of solid carbon dioxide to the boiling point of oxygen, and the research owed much to the patient and assiduous co-operation of Mr. Sidney Young. It was found that the influence of temperature effects great alterations in the specific heat of different metals, and the assumption of a constant atomic heat at the absolute zero had to be abandoned. The concluding section of this inquiry, published in 1904, was directed to testing the validity of Neumann's law which assumes that when an atom undergoes chemical combination it retains that capacity for heat which is displayed in the elemental state, and for this purpose the tellurides of nickel, tin and silver were examined, along with silver–aluminium alloy. The results were interpreted as indicating that Neumann's law may be regarded as approximately valid for specific heats at all temperatures, and that specific heat is not a measure of work done in separating the molecules of a substance, but is determined almost entirely by the nature of the atoms composing the physical molecules. A final summary of contemporary knowledge relating to this field was made the subject of Tilden's second presidential address to the Chemical Society (1905).

In this division also must be grouped the paper on "Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid" (1896), in which it was shown that these familiar derivatives of phosphorus are P_4O_{10} and $H_2P_2O_6$. Thus it will be recognised that the scope of his research was wide and that, in common with those of other active workers at a time when boundaries between the organic and inorganic branches were less rigid, and when physical chemistry was unknown, his interests embraced a variety of topics. This was reflected in the freedom he ungrudgingly gave to his staff and students in choosing their own subjects for research, leading to a great diversity in production from the department under his control. Until a late period of his life he remained unreconciled to such divisions of classification and technique as had then inevitably asserted themselves, and he continued to be a true chemical philosopher to the end. His earlier books, "Introduction to Chemical Philosophy" (1876), "A Manual of Chemistry" (1896), and "A Short History of the Progress of Scientific Chemistry" (1899), were characteristic of this attitude, which appeared also in the Cannizzaro Memorial Lecture delivered on June 26th, 1912, and the first presidential address of March, 1904, when he reviewed the state of knowledge and theory during the early years of the Chemical Society. A chemist with these tastes, present at scientific meetings with regularity since his first attendence in 1862, and recalling a lecture by Berthelot on "Synthetic Methods in Organic Chemistry" (June 4th, 1863), had indeed a mine of material upon which to draw.

A dispassionate survey of Sir William Tilden's life leads easily to the conclusion that he was a self-made man in the finest interpretation of the title: and the product was fine. Hampered by early disadvantages, he overcame them by determination and industry. Without useful friends in early life, he made them; and made them by those qualities of character that make the best. Threatened by submergence in a humdrum occupation, he looked below the surface of his materials and found that which enabled him to rise high above their surface, and to vivify the materials themselves. Becoming a teacher through the chance by which science-teaching is almost the only shelter for the potential investigator, he remained faithful to the calling which gave him that shelter, continuing as an active and conscientious teacher during forty-six years. Imbued with a profound interest in all aspects of chemistry, historical, human, and philosophical, but free from ostentation or flamboyance, his teaching prospered more by graceful and accurate presentation than by personal magnetism. Drift of circumstances involved him in two pioneer movements, the founda-

tion of a modern side to a great public school, and the construction of a science-school which became a great university: both movements were substantially furthered by his personality and persistence. These qualities he devoted also to the service of chemistry as a profession, in a degree which few chemists have attained, his association with the Chemical Society and the Institute of Chemistry bearing witness to this loyalty. Throughout a laborious career, oppressed by early difficulties and clouded at times by domestic affliction, he cherished a fine appreciation of the graces which life offers, and enjoyed their consolations with evident gratitude. Into the common dealings of every day there was woven that shade of dignity which has now become old-fashioned, but remains precious; it was entirely unaffected, and untouched by vanity or coldness; because, underlying it, as his intimates were well aware, ran a strong current of generosity and affection.

M. O. F.

WILLIAM CARLETON WILLIAMS.

BORN AUGUST 17TH, 1850; DIED MAY 25TH, 1927.

TWENTY-THREE years ago W. Carleton Williams retired from the Professorship of Chemistry in the University College, Sheffield, a position to which he was appointed in 1883, in succession to Carnelley, the first Professor of Chemistry in the Firth College, which subsequently became the University College, Sheffield.

Firth College was founded by the munificence of Mark Firth, and was opened by Prince Leopold in 1879. Its history, like that of other similar institutions of that period, was, during the first decade of its existence, an unbroken struggle against financial difficulties and restricted conditions. The Technical Education Act of 1889, and the beginning of the Government grants to University Colleges to enable them to develop also on the side of the humanities and pure science, combined to mitigate the severity of the struggle. The next decade witnessed the development of a movement for co-operation between Firth College, the Medical School, which was founded in 1828, and the Technical School, a rate-supported institution. The incorporation of these three bodies, and the raising of an endowment fund, as a memorial of the visit of Queen Victoria to Sheffield, in the year of the Diamond Jubilee, resulted in the grant of a Charter to the new University College in May 1897. The breaking up of the Victoria University, with the immediate result of the creation of the Universities of Liverpool and of Manchester, and later that of Leeds, resulted, naturally, in the desire for a similar recognition and status on behalf of the University College in Sheffield.



W. Carleton Williams

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In addition to the funds already subscribed for buildings, a call was made for an endowment fund of £100,000 to secure the desired recognition. The successful issue of this effort was the grant, in May 1904, of a University Charter.

Carleton Williams' twenty-one years' tenure of the Firth Chair of Chemistry were momentous years in the development of the College; he not only shared to the full in the anxieties and activities of that period, but contributed generously to the funds raised from time to time, and to the University Endowment Fund he subscribed a year's salary.

The advancement of the College to University status and the approaching completion of the Chemical Laboratory in the new buildings, with the design and arrangement of which he had busied himself, appeared to Williams a suitable opportunity to put into effect his contemplated resignation, thus giving his successor a perfectly free hand. The College Council on receiving his resignation passed the following resolution: "That in accepting with great regret the resignation of Professor W. Carleton Williams of the Firth Chair of Chemistry, the Council desires to place on record its appreciation of the valuable services which he has rendered to the College during his 21 years' connection with the College."

Carleton Williams received his chemical training at the Owens College, Manchester, under Dr. Roscoe (later Sir Henry), entering the College in 1866, in his seventeenth year. His course of study was crowned by the award, in 1871, of the Dalton Chemical Scholarship, for which he presented an account of the results of an investigation on the oxychlorides of antimony (*Mem. Manchester Phil. Soc.*, 1872, 3; 1876, 61). In the same year he was elected an Associate of Owens College. As Dalton Scholar, in accordance with the tradition of those days, Williams went to Germany, where he continued his studies, working first in Bunsen's laboratory at the University of Heidelberg and then, in the second year, at the University of Bonn, where Kekulé directed the Chemical Department. In Bonn he devoted himself to extending his knowledge of organic chemistry, and an outcome of this period was the publication in the *Berichte*, "Ueber Terebinsäure und Pyroterebinsäure" (1873, **6**, 1094). Amongst his fellow students at Bonn were van 't Hoff, Claisen, Königs, Bernthsen, and Wallach, who became *Privat-docent*, then Extra-ordinary Professor, and later Professor of Chemistry in the University of Göttingen.

Returning to Manchester in 1873, Williams was appointed Demonstrator in Chemistry, thus commencing his teaching career in the first session in the new buildings, to which the Owens College had been transferred from the original quarters in Quay Street.

At this time the staff of the Chemical Department consisted, in addition to Professor Roscoe, of C. Schorlemmer, as Lecturer in Organic Chemistry, W. Dittmar as Lecturer in Chemistry, and W. Carleton Williams and H. Grimshaw, Demonstrators. The ten years spent at Owens College were years in which, with laboratory teaching, day and evening classes, and tutorial classes, "full-time" was literally interpreted, and time for research was only to be secured in snatches and by dedicating portions of the vacation to such work.

During this period Williams published the following papers: The Derivatives of Di*iso*butyl (J., 1877, **31**, 541; 1879, **35**, 541); Stannic Arsenate (*Mem. Manchester Phil. Soc.*, 1876, 67); On some Compounds of Antimony Pentachloride with Ethyl Alcohol and with Ether (J., 1876, **29**, 463). With Carnelley he conducted an investigation, the results of which were communicated to this Society, *viz.*: On the Determination of High Boiling Points (J., 1878, **33**, 281); On the Boiling Points of Certain Metals and Metallic Salts (J., 1879, **35**, 563); The Melting and Boiling Points of Certain Inorganic Substances (J., 1880, **37**, 125); and in conjunction with the writer a paper "*Ueber die Bestimmung des specifischen Brechungs-Vermögens festen Körper in ihren Lösungen*" (*Ber.*, 1881, **14**, 2549), which formed part of the report of the British Association Committee on Refraction of Solids: Determining Specific Refractions of Solids from their Solutions.

In the course of an investigation on the sulphides of phosphorus Williams met with a serious accident due to an explosion, in which he was badly burnt on the face, head and hands; fortunately the eyes were not permanently affected.

After the granting of the Charter creating the Victoria University, Williams was made a Lecturer in Chemistry in the University, and in recognition of his standing as an Associate of Owens College, was admitted to the degree of B.Sc. at the first graduation ceremony of the University in 1882.

The translation of Lothar Meyer's "*Die Modernen Theorien der Chemie*," undertaken by Williams in association with the writer, was published in 1888, and was followed in 1892 by the translation of Lothar Meyer's "*Grundzüge der theoretischen Chemie.*"

At Sheffield, Williams devoted himself to teaching and the development of his department. An epidemic of lead poisoning in Sheffield led to an investigation of the action of water on lead, and to the volume published to commemorate the incorporation of the University College at Sheffield he contributed an account of his extensive examination of the distribution of carbonic acid in the air.

Further, the results of his examination of methods for the deter-

mination of zinc formed part of the Report of the British Association Committee on Electrolytic Methods of Quantitative Analysis, published in 1898.

On leaving Sheffield Williams moved to the south and settled at Goring-on-Thames, where Mrs. Williams and he found congenial occupation in tending and developing their garden. Archæology claimed his interest, and he became a member of the British Archæological Association and of the Berkshire Archæological Society, the meetings of which and the Summer Congress he attended regularly. In fact a fortnight before his death he took part in an excursion of the Association to Dunstable. He served for some years on the Council of the British Archæological Association.

In his earlier days Williams found considerable pleasure and recreation in tramping, and thus acquired an intimate knowledge of the Lake District, North Wales and other parts of the country, and in like manner gained an acquaintance with the Rhineland, Switzerland, the Bavarian Alps, the Dolomites and other districts in Europe. The writer retains pleasant recollections of many such tramps, made in his company. Travel always appealed to Williams and he had visited most of the capital towns of Europe, and also Canada and the United States of America. From early manhood he was liable to attacks of gout and it was during one of these attacks that he passed away on May 25th of this year.

William Carleton Williams was born at Salford on August 17th, 1850; in 1883 he married Miss S. E. Andrews, who with their daughter, Ethel Carleton, survives him. Miss Carleton Williams graduated in the History Schools at Oxford and is the authoress of several clever and interesting books dealing with her experiences and travels.

The Jubilee of Williams's Fellowship of the Chemical Society occurred three years ago, for he was elected in 1874; he served for many years on the staff of Abstractors for the Journal; in 1894 he was elected a Fellow of the Institute of Chemistry, and since 1877 was a Member of the British Association. Under his will the Chemical Society is a beneficiary, as are also the Faculty of Science of the University of Sheffield, the Chemical Department of the University of Manchester, and the Benevolent Fund of the Institute of Chemistry.

P. Phillips Bedson.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_4 Methane, propagation of flame in mixtures of air and (CHAPMAN and WHEELER), 38.

CO Carbon monoxide, decomposition of, in the corona discharge (LUNT and VENKATESWARAN), 857; explosions of air and (ELLIS and WHEELER), 156; ignition of mixtures of hydrogen and air (MAXWELL, PAYMAN, and WHEELER), 297.

CO_2 Carbon dioxide, determination of, in soil solutions (FLINT), 2975.

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CH_2O Formaldehyde, condensation of, with glyoxalines (GRINDLEY and PYMAN), 3128.

$COCl_2$ Carbonyl chloride, thermal dissociation of (INGLESON), 2244.

1 III

CHNS Thiocyanic acid, ferric salt (BAILEY), 2065.

CH_6ON_4 Carbohydrazide, reactions of (BROWN, PICKERING, and WILSON), 107.

C_2 Group.

C_2H_2 Acetylene, action of nitric acid on (MCKIE), 962.

C_2H_4 Ethylene, action of nitric acid on (MCKIE), 962.

2 II

$C_2H_2O_4$ Oxalic acid, formation of, from sugars (CHALLENGER, SUBRAMANIAM, and WALKER), 200; (WALKER, SUBRAMANIAM, and CHALLENGER), 3044.

$C_2H_4O_2$ Acetic acid, purification of (ORTON and BRADFIELD), 983; equilibria of, with its copper and lead salts and water (SANDVED), 2967.

C_2H_5I Ethyl iodide, preparation of (JONES and GREEN), 928.

C_2H_6O Ethyl alcohol, surface tension of (MILLS and ROBINSON), 1823; dehydration of (SMITH), 1288; effect of temperature on solubility in aqueous mixtures of (WRIGHT), 1334; determination of water in (SMITH), 1284.

2 III

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$C_2H_2O_6Mo$ Oxalomolybdous acid, barium salt (JAMES and WARDLAW), 2152.

2 IV

$C_2H_2O_2ClI$ Chloroiodoacetic acid, resolution of, and its salts (McMATH and READ), 537.

$C_2H_8ON_2Cu$ Ethylenediamminocupric hydroxide, hydrated sulphite of (MORGAN and BURSTALL), 1266.

C_3 Group.

C_3O_2 Carbon suboxide, properties of (EDWARDS and WILLIAMS), 855.

3 II

C_3H_6O Acetone, autocatalytic reaction between iodine and (DAWSON), 458.

$C_3H_6O_2$ Methyl acetate, vapour pressures of mixtures of, with water and with sucrose and water (McKEOWN and STOWELL), 97.

$C_3H_6O_3$ *dl*-Glyceraldehyde, preparation and properties of (REEVES), 2477.

C_3H_9N Trimethylamine, action of, with benzyl and nitrobenzyl chlorides (McCOMBIE, SCARBOROUGH, and SMITH), 802.

3 III

C_3H_3OBr α-Bromoacraldehyde (FARMER and HEALEY), 1066.

$C_3H_9N_2Br$ β-Bromo-$\alpha\gamma$-diaminopropane, complex nickel salts of (MANN), 2912.

$C_3H_5N_3S$ *S*-Ethylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2529.

$C_3H_{10}ON_2$ $\alpha\gamma$-Diamino*iso*propyl alcohol, complex nickel salts of (MANN), 2913.

3 IV

$C_3H_4O_3N_2S$ Glyoxaline-2-sulphonic acid, and its barium salt (BARNES and PYMAN), 2712.

$C_3H_3ClI_2Hg_3$ Substance, from mercuric chloride and magnesium methyl iodide (HENRY and SHARP), 1949.

$C_3H_{11}N_3Cl_4Pt$ Trichlorotriaminopropaneplatinic chloride (MANN), 1231.

$C_3H_{12}N_3Cl_5Pt$ Tetrachloro(triaminopropanehydrochloride)platinum (MANN), 1229.

3 V

$C_3H_{10}ONCl_4Mo$ Trimethylammonium molybdenyl tetrachloride (JAMES and WARDLAW), 2151.

C_4 Group.

$C_4H_6O_3$ Acetic anhydride, action of bromine on (ORTON, WATSON, and HUGHES), 2458; (WATSON), 3065; estimation of, in acetic acid (ORTON and BRADFIELD), 983.

$C_4H_6O_8$ Dihydroxytartaric acid, action of halogenated phenylhydrazines on (CHATTAWAY and HUMPHREY), 1323; action of tolylhydrazines on (CHATTAWAY and HUMPHREY), 2793.

$C_4H_8O_2$ Ethyl acetate, hydrolysis of (DAWSON and LOWSON), 2107, 2444.

$C_4H_{10}O$ Ethyl ether, viscosity of, at low temperatures (ARCHIBALD and URE), 610; propagation of flame in mixtures of air and (WHITE), 498; action of, on silicon tetrachloride (KIPPING and MURRAY), 2734.

$C_4H_{12}N_2$ β-Methyltrimethylenediamine, dihydrohalides and complex salts of (MANN), 2916.

4 III

$C_4H_4O_2Cl_2$ Succinylchloride, surface tension and density of (GARNER and SUGDEN), 2880.

$C_4H_4O_5Hg_3$ Substance, from heating mercuric acetate and sodium acetate (MARSH and STRUTHERS), 2659.

$C_4H_6O_6Cu$ Cupriglycollic acid, sodium salt (WARK), 1757.

$C_4H_6O_2S_2$ β-Dithian dioxide (BELL and BENNETT), 1801.

$C_4H_9N_3S$ *S*-Allylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2529.

$C_4H_{10}OS$ Methyl γ-hydroxypropyl sulphide (BENNETT and HOCK), 2498.

$C_4H_{10}O_2S_2$ Dimethylethylene disulphoxides (BELL and BENNETT), 1803.

$C_4H_{10}O_3S$ α-Methylpropanesulphonic acid, and its salts (EVANS, MABBOTT, and TURNER), 1167.

$C_4H_{10}NCl$ β-Chlorodimethylethylamine, picrate of (HANHART and INGOLD), 1013.

$C_4H_{11}N_3S$ *S*-Propylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2529.

4 IV

$C_4H_5ON_2Br$ Bromohydroxymethylglyoxaline, and its hydrochloride (GRINDLEY and PYMAN), 3131.

$C_4H_5OCl_2Br$ αβ-Dichloro-β-bromovinyl ethyl ether (SMITH), 1100.

$C_4H_5OCl_2Br_3$ αβ-Dichloro-αββ-tribromodiethyl ether (SMITH), 1101.

C_4H_6ONCl γ-Chloro-α-hydroxy-*n*-butyronitrile (CRAWFORD and KENYON), 400.

$C_4H_6O_3N_2S$ Methylglyoxaline-2-sulphinic acid (BALABAN and KING), 1871.

$C_4H_6O_3N_2S$ Methylglyoxaline-2-sulphonic acid, and its salts (BALABAN and KING), 1872.

4(5)-Methylglyoxaline-5(4)-sulphonic acid, and its salts (BARNES and PYMAN), 2713.

$C_4H_9O_4SNa$ Sodium *sec.*-butyl sulphate (EVANS, MABBOTT, and TURNER), 1167.

$C_4H_{16}ON_4Cu$ Bisethylenediamminocupric hydroxide, salts of (MORGAN and BURSTALL), 1264.

C_5 Group.

$C_5H_{11}N$ Piperidine, use of, as an alkaline buffer (PRIDEAUX and GILBERT), 2164; as a reagent for halogenonitro-compounds (LE FÈVRE and TURNER), 1113.

$C_5H_{13}N$ Dimethyl-*n*-propylamine, and its picrate (HANHART and INGOLD), 1007, 1019.

5 III

$C_5H_5O_2Br$ Bromo-β-vinylacrylic acid (FARMER and HEALEY), 1063.

$C_5H_6O_2Br_2$ Dibromovinylacrylic acid (FARMER and HEALEY), 1062.

$C_5H_8ON_2$ 1-Methyl-2-hydroxymethylglyoxaline, and its picrate (GRINDLEY and PYMAN), 3135.

C_5H_8OS Penthian-4-one (BENNETT and SCORAH), 198.

$C_5H_{12}O_3N_4$ Diacetyl δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 110.

$C_5H_{13}N_3S$ *S*-Butylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2530.

5 IV

$C_5H_6O_2N_2S$ 2-Thiolmethylglyoxalinecarboxylic acid (BALABAN and KING), 1865.

C_5H_9ONS Penthian-4-one oxime (BENNETT and SCORAH), 199.

5 V

$C_5H_5O_2N_2SAu$ 2-Aurothiolmethylglyoxalinecarboxylic acid (BALABAN and KING), 1870.

$C_5H_4O_2NCl_2Mo$ Pyridinium molybdenum dioxydichloride (JAMES and WARDLAW), 2153.

$C_5H_{11}O_4N_3Cl_2Pt$ Chloro-oxalatotriaminopropaneplatinic chloride (MANN), 1232.

$C_5H_{10}O_4N_3Cl_4Pt$ Tetrachloro(triaminopropanehydrogenoxalate)platinum (MANN), 1231.

5 VI

$C_5H_5O_2N_2ClSHg$ 2-Chloromercurithiolmethylglyoxalinecarboxylic acid (BALABAN and KING), 1871.

C_6 Group.

C_6H_6 Benzene, adsorption of vapour of, by glass, quartz, or platinum (LENHER), 272; partition of hydrochloric acid between water and (KNIGHT and HINSHELWOOD), 466.

$\Delta^{\alpha\epsilon}$-Hexadien-γ-in (FARMER, LAROIA, SWITZ, and THORPE), 2948.

C_6H_8 Hexatriene, structure and behaviour of (FARMER, LAROIA, SWITZ, and THORPE), 2937.

C_6H_{12} *cyclo*Hexane, photobromination of (WOOD and RIDEAL), 2466.

6 II

$C_6H_4O_2$ *p*-Benzoquinone, surface tension and density of (GARNER and SUGDEN), 2880.

C_6H_5Cl Benzyl chloride, action of trimethylamine with (MCCOMBIE, SCARBOROUGH, and SMITH), 802.

C_6H_6O Phenol, condensation of, with chloral (CHATTAWAY and MORRIS), 2013.

$C_6H_6O_2$ Quinol, crystal structure of (CASPARI), 1093.

Resorcinol, condensation of, with cinnamic acid (ELLISON), 1720.

$C_6H_6O_3$ Pyrogallol, condensation of, with cinnamic acid (ELLISON), 1720.

C_6H_7N Aniline, influence of salts on solubility of, in water (GLASSTONE, BRIDGMAN, and HODGSON), 635.

C_6H_7Br Bromohexatrienes (FARMER, LAROIA, SWITZ, and THORPE), 2948.

$C_6H_8O_7$ Citric acid, formation of, from sugars (CHALLENGER, SUBRAMANIAM, and WALKER), 200; (WALKER, SUBRAMANIAM, and CHALLENGER), 3044.

$C_6H_8Br_2$ Dibromohexadienes (FARMER, LAROIA, SWITZ, and THORPE), 2949.

$C_6H_8Br_4$ $\alpha\beta\gamma\delta$-Tetrabromo-Δ^{ϵ}-hexene (FARMER, LAROIA, SWITZ, and THORPE), 2948.

$C_6H_9Br_3$ Tribromohexene (FARMER, LAROIA, SWITZ, and THORPE), 2947.

$C_6H_{10}O_2$ γ-Ethoxycrotonaldehyde (FARMER, LAROIA, SWITZ, and THORPE), 2952.

$C_6H_{10}O_3$ Ethyl acetoacetate, action of, with distyryl ketones (HEILBRON and HILL), 918.

$C_6H_{10}O_8$ Mucic acids, salts (PATTERSON and FULTON), 50.

$C_6H_{10}N_2$ 1:2:3-Trimethylglyoxaline, salts of (GRINDLEY and PYMAN), 3134.

$C_6H_{12}O_2$ Caproic acid, poisoning of charcoal surfaces with (WRIGHT), 2325.

$C_6H_{12}O_6$ Dextrose, mutarotation of, in aqueous alcohols (RICHARDS, FAULKNER, and LOWRY), 1733.

Galactose, structure of (HAWORTH, HIRST, and JONES), 2428.

Lævulose, structure of (HAWORTH, HIRST, and LEARNER), 1040.

$C_6H_{14}O_2$ *s*-Divinylglycol (FARMER, LAROIA, SWITZ, and THORPE), 2946.

$C_6H_{14}O_6$ Dimethyl γ-mannonolactone (GOODYEAR and HAWORTH), 3143.

$C_6H_{15}N$ Dimethyl*iso*butylamine, and its picrate (HANHART and INGOLD), 1017.

$C_6H_{16}N_2$ β-Aminotriethylamine, complex nickel salts of (MANN), 2910.

Dimethylethylethylenediamine, dipicrate of (HANHART and INGOLD), 1010.

6 III

$C_6H_4O_3S$ Thionylpyrocatechol (GREEN), 501.

$C_6H_4N_6Fe$ Hydroferrocyanic acid, calcium and sodium salts, equilibrium of water and (FARROW), 1153; potassium salt, solubility of, in water (VALLANCE), 1328.

C_6H_5OCl *m*-Chlorophenol, Reimer–Tiemann reaction with (HODGSON and JENKINSON), 1740.

$C_6H_5O_3N$ *o*-Nitrophenol, iodination of (HODGSON), 1141.

$C_6H_6O_3N_2$ 3-Nitro-2-aminophenol (KING), 1058.
$C_6H_7O_2Br$ Bromosorbic acid (FARMER and HEALEY), 1064.
Methyl bromo-*p*-vinylacrylate (FARMER and HEALEY), 1063.
C_6H_7NS *o*-Aminothiophenol, condensation of, with $\alpha\beta$-unsaturated acids (MILLS and WHITWORTH), 2738.
$C_6H_8O_2Br_2$ Methyl β-vinylacrylate (FARMER and HEALEY), 1062.
$C_6H_{10}ON_2$ Dimethylhydroxymethylglyoxalines, and their salts (GRINDLEY and PYMAN), 3132.
$C_6H_{10}O_6Cu$ Cuprilactic acid, sodium salt (WARK), 1757.
$C_6H_{10}N_2S$ 2-Ethylthiolmethylglyoxaline, and its salts (BALABAN and KING), 1866.
$C_6H_{12}O_4N_2$ *l*-Dimethoxysuccinamide (HAWORTH and JONES), 2352.
$C_6H_{13}ON$ β-Hydroxylamino-$\beta\gamma$-dimethyl-$\Delta\gamma$-butene, hydrochloride of (EARL and KENNER), 2142.
4-Hydroxy-1-methylpiperidine, and its salts (MILLS, PARKIN, and WARD), 2622.
$C_6H_{13}O_4N$ Hydroxydimethoxybutyramide (AVERY, HAWORTH, and HIRST), 2313.
$C_6H_{13}N_3S$ Acetone *s*-ethylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2529.
$C_6H_{14}NCl$ β-Chlorodimethyldiethylamine, picrate of (HANHART and INGOLD), 1014.
$C_6H_{15}ON$ β-Hydroxydimethyldiethylamine, picrate of (HANHART and INGOLD), 1013.
$C_6H_{19}O_9N_8$ Picratopentamminocobaltic hydroxide, picrates of (DUFF and BILLS), 2371.

6 IV

$C_6HO_4Cl_5S_2$ *s*-Trichlorobenzenedisulphonyl chloride (DAVIES and POWELL), 1124.
$C_6H_3O_7N_3I$ 3-Iodo-2:4:6-trinitrophenol (HODGSON and MOORE), 635.
$C_6H_3O_2NCl_2$ 3:5-Dichloro-4-nitrosophenol[-quinone-4-oxime] (HODGSON and WIGNALL), 2219.
$C_6H_3O_3NCl_2$ 3:5-Dichloronitrophenols (HODGSON and WIGNALL), 2218.
$C_6H_3O_5N_2I$ 3-Iododinitrophenols, and their silver salts (HODGSON and MOORE), 634.
$C_6H_3O_6Cl_3S$ *s*-Trichlorobenzenedisulphonic acid, and its salts (DAVIES and POWELL), 1124.
$C_6H_4O_2NCl$ Nitrobenzyl chloride, action of trimethylamine with (MCCOMBIE, SCARBOROUGH, and SMITH), 802.
$C_6H_4O_3NI$ 3-Iodonitrophenols, and their salts (HODGSON and MOORE), 632.
$C_6H_4O_4Cl_2S_2$ Dichlorothionylquinol (GREEN), 502.
$C_6H_4O_6Cl_2S_2$ 1:3-Dichlorobenzene-4:6-disulphonic acid, and its salts (DAVIES and POOLE), 1122.
$C_6H_5ONCl_2$ 3:5-Dichloroaminophenols (HODGSON and WIGNALL), 2218.
$C_6H_5O_3BrSe$ Bromobenzene-*p*-seleninic acid (PORRITT), 29.
$C_6H_5O_3NHg_5$ Substance, from mercuretin and ammonia (MARSH and STRUTHERS), 2660.
$C_6H_7O_3N_2Br$ α-Bromomuconamides (FARMER and DUFFIN), 408.
$C_6H_8O_2NCl$ γ-Chloro-α-cyanopropyl benzoate (CRAWFORD and KENYON), 400.
$C_6H_9O_4N_2As$ 3:5-Diamino-2-hydroxyphenylarsinic acid (KING), 1057.
$C_6H_{11}ON_3S$ Penthian-4-one semicarbazone (BENNETT and SCORAH), 199.
$C_6H_{11}OIS$ Penthianonemethylsulphonium iodide (BENNETT and SCORAH), 200.
$C_6H_{12}O_2N_2S$ Thiodipropiondiamide (BENNETT and SCORAH), 196.
$C_6H_{13}NClI$ β-Chlorodimethyldiethylammonium iodide (HANHART and INGOLD), 1014.

6 V

$C_6H_5O_4N_2Cl_3S_2$ *s*-Trichlorobenzenedisulphonamide (DAVIES and POOLE), 1124.

$C_6H_{20}ON_2Cl_5Mo$ Ditrimethylammonium molybdenyl pentachloride (JAMES and WARDLAW), 2148.

C_7 Group.

$C_7H_6O_2$ Benzoic acid, heats of combustion of salicylic acid and (BERNER), 338; equilibrium of sulphur with (HAMMICK and HOLT), 493; nitration of (COOPER and INGOLD), 840.

Toluquinone, surface tension and density of (GARNER and SUGDEN), 2880.

$C_7H_6O_3$ *p*-Hydroxybenzoic acid, condensation of chloral with (CHATTAWAY and PRATS), 685.

Salicylic acid, heats of combustion of benzoic acid and (BERNER), 338; copper salt, transport numbers of (HAMER and BURY), 333; molybdenyl salts, isomeric (WARDLAW and WORMELL), 137.

$C_7H_8O_3$ ω-Methoxy-5-methylfurfural (HAWORTH, HIRST, and NICHOLSON), 1524.

$C_7H_8O_4$ ω-Methoxy-5-methylfuran-2-carboxylic acid (HAWORTH, HIRST, and NICHOLSON), 1525.

$C_7H_{17}N$ Dimethylethyl-*n*-propylamine, salts of (HANHART and INGOLD), 1006.

Trimethyl*iso*butylamine, picrate of (HANHART and INGOLD), 1017.

7 III

$C_7H_3OCl_3$ 2:3:5-Trichlorobenzaldehyde (HODGSON and BEARD), 2382.

$C_7H_3O_8N_3$ 2:4:6-Trinitro-3-hydroxybenzaldehyde (HODGSON and BEARD), 2379.

$C_7H_4OBr_2$ 3:4-Dibromobenzaldehyde (HODGSON and BEARD), 26.

$C_7H_4OI_2$ 3:4-Di-iodobenzaldehyde (HODGSON and BEARD), 27.

$C_7H_4O_2Br_4$ Substance, from bromine and dimethylpyrone (COLLIE and KLEIN), 2163.

$C_7H_4O_6N_2$ Dinitrohydroxybenzaldehydes, and their salts (HODGSON and BEARD), 2378.

C_7H_5OCl Benzoyl chloride, nitration of (COOPER and INGOLD), 839.

$C_7H_5O_2Cl$ Chlorohydroxybenzaldehydes (HODGSON and JENKINSON), 1740.

$C_7H_5O_2I$ Iodohydroxybenzaldehydes (HODGSON and JENKINSON), 3043.

$C_7H_5O_3Cl$ 2-Chloro-4-hydroxybenzoic acid (HODGSON and JENKINSON), 1742.

$C_7H_5O_3Br$ Bromohydroxybenzoic acids (HODGSON and JENKINSON), 3042.

$C_7H_5O_3I$ Iodohydroxybenzoic acids (HODGSON and JENKINSON), 3043.

C_7H_5NSe Benzselenazole (CLARK), 2806.

$C_7H_6O_2Br_2$ Substance, from heating $C_{14}H_{17}O_4Br_3$ with water (COLLIE and KLEIN), 2162.

$C_7H_6O_3N_2$ Nitrobenzaldoximes, and their sulphates (BRADY and WHITEHEAD), 2935.

$C_7H_6O_5N_2$ Dinitro-*p*-cresols (DADSWELL and KENNER), 584.

C_7H_7ON Benzamide, nitration of (COOPER and INGOLD), 841.

C_7H_7OCl *o*-Chloroanisole, nitration of (INGOLD and SMITH), 1691.

C_7H_7OBr *o*-Bromoanisole, nitration of (INGOLD and SMITH), 1694.

C_7H_7OI *o*-Iodoanisole, nitration of (INGOLD and SMITH), 1695.

C_7H_7OK Potassium *m*-tolyloxide, interaction of aliphatic esters with (SMITH), 170.

$C_7H_7O_2Br$ Bromoquinol methyl ethers (IRVINE and SMITH), 74.

$C_7H_7O_3N$ Acetyl-α-furfuraldoxime (BRADY and GOLDSTEIN), 1961.

$C_7H_7O_3N_3$ 3-Nitro-4-aminobenzaldoxime (HODGSON and BEARD), 23.

$C_7H_7O_3Br$ Substance, from bromine and diacetylacetone salts (COLLIE and KLEIN), 2164.

$C_7H_8O_3S$ Toluene-ω-sulphonic acid, nitration of (BOTTOMLEY and ROBINSON), 2786.

$C_7H_8O_2Se$ Tolueneseleninic acids (PORRITT), 29.

$C_7H_8O_3N_2$ *O-p*-Nitrobenzylhydroxylamine, and its hydrochloride (BRADY and KLEIN), 882.
$C_7H_9O_2Br$ Methyl bromosorbate (FARMER and HEALEY), 1064.
$C_7H_9O_3N$ ω-Methoxy-5-methylfurfuraldoxime (HAWORTH, HIRST, and NICHOLSON), 1524.
$C_7H_{10}O_2Br_2$ Methyl dibromosorbate (FARMER and HEALEY), 1064.
$C_7H_{11}O_2N$ ββ-Dimethylglutarimide (SIRCAR), 604.
αs-Methylethylsuccinimide (SIRCAR), 1254.
$C_7H_{12}N_2S$ Acetone *S*-allylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2529.
$C_7H_{14}ON_4$ Diacetonecarbohydrazone (BROWN, PICKERING, and WILSON), 108.
$C_7H_{15}O_2N$ Carnitine, constitution of (CRAWFORD and KENYON), 396.
$C_7H_{15}N_2S$ Acetone *S*-propylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2529.

7 IV

$C_7H_3O_4NCl_2$ 2:5-Dichloro-3-nitrobenzoic acid (HODGSON and BEARD), 2381.
$C_7H_3NBr_2S$ 2:5-Dibromophenylthiocarbimide (DYSON, GEORGE, and HUNTER), 443.
$C_7H_4ON_2Br_4$ 2:4:5:6-Tetrabromo-3-aminobenzaldoxime (HODGSON and BEARD), 2427.
$C_7H_4O_3NI$ 4-Iodo-3-nitrobenzaldehyde (HODGSON and BEARD), 25.
C_7H_4NIS Iodophenylthiocarbimides (DYSON, GEORGE, and HUNTER), 443.
$C_7H_5ONBr_2$ 3:4-Dibromobenzaldoxime (HODGSON and BEARD), 26.
$C_7H_5ONI_2$ 3:4-Di-iodobenzaldoxime (HODGSON and BEARD), 27.
$C_7H_5OCl_2I$ Dichloroiodoanisole (INGOLD, SMITH, and VASS), 1249.
$C_7H_5O_2NCl_2$ 2:4-Dichloro-5-nitrotoluene (DADSWELL and KENNER), 585.
$C_7H_5O_2N_3S$ 3-Nitro-1-aminobenzthiazole (DYSON, HUNTER, and MORRIS), 1192.
$C_7H_5O_3NCl_2$ 3:5-Dichloronitroanisoles (HODGSON and WIGNALL), 2219.
$C_7H_5O_3N_2Cl$ 4-Chloro-3-nitrobenzaldoxime (HODGSON and BEARD), 24.
$C_7H_5O_3N_2I$ 4-Iodo-3-nitrobenzaldoxime (HODGSON and BEARD), 25.
$C_7H_5N_2ClS$ 5-Chloro-1-aminobenzthiazole (DYSON, HUNTER, and MORRIS), 1190.
$C_7H_5N_2Br_5S$ 5-Bromo-1-aminobenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1191.
C_7H_6ONCl α-*o*-Chlorobenzaldoxime, sulphate of (BRADY and WHITEHEAD), 2936.
C_7H_6ONI Iodohydroxybenzaldoximes (HODGSON and JENKINSON), 3043.
C_7H_6OClI 4-Chloro-2-iodoanisole (INGOLD, SMITH, and VASS), 1248.
$C_7H_6O_2NCl$ Chlorohydroxybenzaldoxime (HODGSON and JENKINSON), 1740.
3-Chloro-4-nitroanisole (HODGSON and WIGNALL), 2220.
$C_7H_6O_3NI$ 3-Iodonitrophenyl methyl ethers (HODGSON and MOORE), 632.
$C_7H_6N_2Br_2S$ 2:5-Dibromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.
$C_7H_7ONCl_2$ 3:5-Dichloro-4-aminoanisole (HODGSON and WIGNALL), 2219.
$C_7H_7O_2ClS$ Toluene-ω-sulphonyl chloride (BOTTOMLEY and ROBINSON), 2785.
$C_7H_7N_2BrS$ *o*-Bromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.
$C_7H_7N_2IS$ Iodophenylthiocarbamides (DYSON, GEORGE, and HUNTER), 443.
$C_7H_8O_5N_2As$ 2-Hydroxy-4-carbamidophenylarsinic acid, and its salts (KING), 1056.
$C_7H_{10}O_3N_2S$ 2-Ethylthiolmethylglyoxalinecarboxylic acid, and its hydrochlorides (BALABAN and KING), 1867.
$C_7H_{15}ON_2Cl$ γ-Dimethylamino-α-hydroxy-*n*-butyronitrile methochloride, and its salts (CRAWFORD and KENYON), 401.

$C_7H_{16}O_3NCl$ α-Hydroxy-γ-butyrotrimethylbetaine hydrochloride, and its salts (CRAWFORD and KENYON), 401.

7 V

$C_7H_5ONClBr$ Chlorobromobenzaldoximes (HODGSON and BEARD), 25.

C_7H_5ONClI Chloroiodobenzaldoximes (HODGSON and BEARD), 26.

C_7H_5ONBrI Bromoiodobenzaldoximes (HODGSON and BEARD), 26.

$C_7H_5N_2ClBr_2S$ 5-Chloro-1-aminobenzthiazole dibromide (DYSON, HUNTER, and MORRIS), 1190.

$C_7H_5N_2ClBr_6S$ 5-Chloro-1-aminobenzthiazole hexabromide (DYSON, HUNTER, and MORRIS), 1191.

$C_7H_6O_4NClS$ Nitrobenzylsulphonyl chlorides (C. K. and E. H. INGOLD and SHAW), 831.

$C_7H_9O_2N_2SAu$ Ethyl 2-aurothiolmethylglyoxalinecarboxylate (BALABAN and KING), 1869.

7 VI

$C_7H_9O_2N_2ClSHg$ Ethyl 2-chloromercurithiolmethylglyoxalinecarboxylate (BALABAN and KING), 1871.

C_8 Group.

C_8H_{12} αζ-Dimethylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2957.

8 II

$C_8H_6O_4$ *iso*Phthalic acid, oxidation of (FARMER and RICHARDSON), 62.

$C_8H_8O_3$ Acetylpyrocatechol (GREEN), 502.

Mandelic acid, cupric salt (WARK), 1754.

$C_8H_{10}O_3$ 2:3-Dimethyl*cyclo*butane-1:4-dicarboxylic anhydride (VOGEL), 1993.

$C_8H_{10}O_4$ 4:5-Dimethoxyresorcinol (CHAPMAN, PERKIN, and ROBINSON), 3031.

4-Hydroxy-2:2-dimethyl*cyclo*penten-3-one-1-carboxylic acids (GIBSON, HARIHARAN, and SIMONSEN), 3013.

Methyl ω-methoxy-5-methylfuran-2-carboxylate (HAWORTH HIRST, and NICHOLSON), 1525.

$C_8H_{12}O_2$ Ethyl Δ^1-*cyclo*pentenecarboxylate (SIRCAR), 1255.

*cyclo*Hexylideneacetic acid, sodium salt (LINSTEAD), 370.

3-Hydroxy*cyclo*hexolacetolactone (ROBINSON and ZAKI), 2411.

$C_8H_{12}O_4$ 2:3-Dimethyl*cyclo*butane-1:4-dicarboxylic acids (VOGEL), 1993.

Methyl Δβ-dihydromuconate (FARMER and DUFFIN), 409.

Methylethylparaconic acid, and its silver salt (SIRCAR), 1258.

*trans-cyclo*Pentane-1-carboxy-2-acetic acid (SIRCAR), 1255.

$C_8H_{12}Br_2$ Dibromo-*s*-dipropenylethylene glycol (FARMER, LAROIA, SWITZ, and THORPE), 2957.

$C_8H_{14}O_2$ β-Methyl-α-ethyl-Δβ-pentenoic acid, and its silver salt (KON and NARAYANAN), 1545.

$C_8H_{14}O_5$ 2:3:4-Trimethyl *l*-arabonolactone (DREW and MACBETH), 778.

Trimethyl arabonolactones (DREW, GOODYEAR, and HAWORTH), 1244.

Trimethyl γ-arabonolactones, oxidation of (HAWORTH, HIRST, and LEARNER), 2432.

Trimethyl xylonolactones (DREW, GOODYEAR, and HAWORTH), 1244.

$C_8H_{16}O_6$ γ-Ethylfructoside (ALLPRESS, HAWORTH, and INKSTER), 1235.

$C_8H_{18}O$ α-Ethoxyhexane (FARMER, LAROIA, SWITZ, and THORPE), 2951.

$C_8H_{20}N_2$ β-Dimethylaminodimethyldiethylamine picrate (HANHART and INGOLD), 1011.

Hexamethylethylenediamine, picrate of (HANHART and INGOLD), 1012.

8 III

$C_8H_3N_3Mo$ Hydromolybdicyanic acid, and its salts (BUCKNALL and WARDLAW), 2987.

$C_8H_4O_2Cl_2$ Phthalyl chlorides, surface tension and density of (GARNER and SUGDEN), 2881.

$C_8H_4N_2Cl_4$ *aa*-Dichloro-*β*-2:4-dichlorobenzeneazoethylene (CHATTAWAY and BENNETT), 2853.

$C_8H_4N_2S$ Cyanophenylthiocarbimides (DYSON, GEORGE, and HUNTER), 442.

$C_8H_4N_3Mo$ Hydromolybdocyanic acid, salts of (BUCKNALL and WARDLAW), 2981.

$C_8H_5O_4N_3$ 2:4-Dinitrophenylacetonitrile (FAIRBOURNE and FAWSON), 48.

$C_8H_6OCl_2$ 3:4-Dichloroacetophenone (ROBERTS and TURNER), 1855.

$C_8H_6O_3Cl_2$ 3:5-Dichloroanisic acid (BLAKEY, JONES, and SCARBOROUGH), 2868.

$C_8H_6O_5N_2$ *α*-6-Nitro-3:4-methylenedioxybenzaldoxime, sulphate of (BRADY and WHITEHEAD), 2937.

$C_8H_6O_6N_2$ Dinitromethoxybenzaldehydes (HODGSON and BEARD), 2381.

$C_8H_6O_7N_2$ 2:3-Dinitro-4-methoxybenzoic acid (DADSWELL and KENNER), 587.

2:6-Dinitro-3-methoxybenzoic acid (HODGSON and BEARD), 2381.

$C_8H_7O_2N$ 2-Hydroxy-5-methoxybenzonitrile (SHINODA), 1984.

$C_8H_7O_2Cl$ 4-Chloro-2-methoxybenzaldehyde (HODGSON and JENKINSON), 1741.

$C_8H_7O_2Br$ Bromomethoxybenzaldehydes (HODGSON and JENKINSON), 3042.

$C_8H_7O_2I$ Iodomethoxybenzaldehydes (HODGSON and JENKINSON), 3043.

$C_8H_7O_3N$ *α*-3:4-Methylenedioxybenzaldoxime, sulphate of (BRADY and WHITEHEAD), 2937.

$C_8H_7O_3N_3$ 7-Nitro-6-methoxyindazole (DADSWELL and KENNER), 586.

$C_8H_7O_3Cl$ 4-Chloro-2-methoxybenzoic acid (HODGSON and JENKINSON), 1741.

$C_8H_7O_3Br$ Bromomethoxybenzoic acids (HODGSON and JENKINSON), 3042.

$C_8H_7O_3I$ Iodomethoxybenzoic acids (HODGSON and JENKINSON), 3043.

$C_8H_7N_3S$ Cyanophenylthiocarbamides (DYSON, GEORGE, and HUNTER), 442.

$C_8H_7Cl_2Br$ *α*-2:4-Dichlorophenylethyl bromide (EVANS, MABBOTT, and TURNER), 1165.

$C_8H_8OCl_2$ 2:4-Dichlorophenylmethylcarbinol (EVANS, MABBOTT, and TURNER), 1164.

$C_8H_8O_4N_2$ Dinitro-*β*-phenylethane (BAKER and WILSON), 846.

$C_8H_8O_6N_2$ 2:5-Dinitrocreosol (OXFORD), 1967.

5:6-Dinitro*iso*creosol (OXFORD), 1970.

$C_8H_9O_2N$ Methoxybenzaldoximes, sulphates of (BRADY and WHITEHEAD), 2936.

α-Nitro-*β*-phenylethane (BAKER and WILSON), 844.

Piperonylmethylamine, and its salts (MALAN and ROBINSON), 2654.

$C_8H_9O_2Cl$ Chlorocreosol (OXFORD), 1966.

$C_8H_9O_3N$ 2-Hydroxy-5-methoxybenzaldoxime (SHINODA), 1984.

$C_8H_9O_4N$ 6-Nitro*iso*creosol (OXFORD), 1970; (HEAP, JONES, and ROBINSON), 2022.

$C_8H_9O_4N_3$ *p*-Nitrobenzyloxycarbamide (BRADY and KLEIN), 882.

$C_8H_9O_4Br$ Methyl *α*-bromomuconates (FARMER and DUFFIN), 407.

$C_8H_{10}ON_4$ Benzaldehyde *δ*-aminosemicarbazone (BROWN, PICKERING, and WILSON), 110.

$C_8H_{10}O_2Se$ Xylene-4-seleninic acids (PORRITT), 29.

$C_8H_{10}O_3N_2$ Nitro-4-methoxytolnidines (DADSWELL and KENNER), 584.

Nitroso-*N*-*o*-methoxybenzylhydroxylamine (BRADY and BENNETT), 897.

$C_8H_{10}O_3S$ Phenylethanesulphonic acids, and their salts (EVANS, MABBOTT, and TURNER), 1161.

$C_8H_{10}O_4Br_2$ Methylmuconate dibromides (FARMER and DUFFIN), 402.

$C_8H_{10}NCl$ Chloro-*m*-2-xylidines (DADSWELL and KENNER), 1106.
$C_8H_{10}NI$ 3-Iododimethylaniline (HODGSON and WIGNALL), 1145.
$C_8H_{11}O_2N$ *trans*-Hexahydrophthalimide (SIRCAR), 1254.
N-*o*-Methoxybenzylhydroxylamine, hydrochloride of (BRADY and BENNETT), 896.
*trans-cyclo*Pentane-1-carboxy-2-acetimide (SIRCAR), 1255.
*cyclo*Pentane*spiro*succinimide (SIRCAR), 1254.
$C_8H_{11}O_2I$ 1-Iodo-2-hydroxy*cyclo*hexylacetic acid γ-lactone (LINSTEAD and MAY), 2572.
$C_8H_{11}O_3N_3$ ω-Methoxy-5-methylfurfural semicarbazone (HAWORTH, HIRST, and NICHOLSON), 1523.
$C_8H_{11}N_3S$ δ-Benzylthiosemicarbazide, and its hydrochloride (BAIRD, BURNS, and WILSON), 2531.
$C_8H_{12}O_3S$ Ethyl penthian-4-one-3-carboxylate (BENNETT and SCORAH), 198.
Ethyl Δ^3-penthien-4-ol-3-carboxylate (BENNETT and SCORAH), 197.
$C_8H_{13}O_2N$ *as*-Diethylsuccinimide (SIRCAR), 1254.
βδ-Methylethylglutarimide (SIRCAR), 604.
$C_8H_{13}O_3N_3$ Δγ-Pentene-*aaε*-tricarboxylamide (FARMER and HEALEY), 1065.
$C_8H_{15}O_3N$ Methylbetaines of 4-hydroxypiperidylacetic acid (MILLS, PARKIN, and WARD), 2623.
$C_8H_{16}O_4N_2$ Dimethoxysuccinomethylamides (HAWORTH and JONES), 2351.
$C_8H_{17}N_3S$ Acetone δ-butylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2530.
$C_8H_{19}N_3S$ δ-Heptylthiosemicarbazide, and its hydrochloride (BAIRD, BURNS, and WILSON), 2533.

8 IV

$C_8H_3N_2Cl_4Br$ *aa*-Dichloro-δ-bromo-β-2:4-dichlorobenzeneazoethylene (CHATTAWAY and BENNETT), 2853.
$C_8H_4N_2Cl_2Br_2$ *aa*-Dichloro-β-2:4-dibromobenzeneazoethylene (CHATTAWAY and BENNETT), 2853.
$C_8H_4N_2Cl_3Br_2$ *aa*-Dichlorochlorobromobenzeneazoethylenes (CHATTAWAY and BENNETT), 2853.
$C_8H_5O_3NCl_2$ 3:4-Dichloro-2-nitroacetophenone (ROBERTS and TURNER), 1855.
$C_8H_5NBr_2S$ 3:5-Dibromo-*o*-tolylthiocarbimide (DYSON, GEORGE, and HUNTER), 444.
$C_8H_5N_3Br_4S$ 1-Amino-5-cyanobenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1189.
$C_8H_5N_3Br_6S$ 1-Amino-5-cyanobenzthiazole hexabromide (DYSON, HUNTER, and MORRIS), 1189.
$C_8H_6O_2N_2Cl_2$ Glyoxylic acid dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2852.
$C_8H_6O_2N_2Br_2$ Glyoxylic acid dibromophenylhydrazone (CHATTAWAY and BENNETT), 2852.
$C_8H_5O_3N_2S$ 3-Nitro-*o*-tolylthiocarbimide (DYSON, GEORGE, and HUNTER), 444.
$C_8H_6O_4NI$ 3-Iodo-6-nitrophenyl acetates (HODGSON and MOORE), 632.
$C_8H_7ONCl_2$ 3:4-Dichloro-2-aminoacetophenone (ROBERTS and TURNER), 1856.
C_8H_7ONS Anisylthiocarbimides (DYSON, GEORGE, and HUNTER), 440.
C_8H_7OClS Chloromethylthiolbenzaldehydes (HODGSON and BEARD), 2427.
$C_8H_7O_3NS$ Nitromethylthiolbenzaldehydes (HODGSON and BEARD), 2425.
C_8H_8ONCl *N*-Chloroacetanilide, action of hydrochloric acid with (SOPER and PEYDE), 2761.
$C_8H_8ON_2S$ 1-Amino-5-methoxybenzthiazole (DYSON, HUNTER, and MORRIS), 1191.

$C_8H_8O_2NCl$ 4-Chloro-2-methoxybenzaldoxime (HODGSON and JENKINSON), 1741.
Chloronitro-*m*-xylenes (DADSWELL and KENNER), 1106.
$C_8H_8O_2NBr$ Bromomethoxybenzaldoximes (HODGSON and JENKINSON), 3042.
$C_8H_8O_2NI$ Iodomethoxybenzaldoximes (HODGSON and JENKINSON), 3043.
$C_8H_8O_2N_3Cl$ Chlorohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 1741.
$C_8H_8O_2N_3Br$ Bromohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 3041.
$C_8H_8O_2N_3I$ Iodohydroxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 3043.
$C_8H_8O_3NCl$ 3-Chloro-6-nitro-4-methoxytoluene (DADSWELL and KENNER), 585.
$C_8H_8O_3N_2S$ Nitromethylthiolbenzaldoximes (HODGSON and BEARD), 2425.
C_8H_8NISe Benzselenazole methiodide (CLARK), 2806.
$C_8H_8N_2Br_4S$ 1-Amino-5-methylbenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1191.
$C_8H_9ON_3I$ 3-Iodo-4-nitrosodimethylaniline (HODGSON and WIGNALL), 1145.
$C_8H_9O_2NS$ 3-Nitroso-4-methylthiolbenzyl alcohol (HODGSON and BEARD), 2426.
$C_8H_9O_2ClS$ Phenylethanesulphonyl chlorides (EVANS, MABBOTT, and TURNER), 1162.
$C_8H_9O_3NS$ Nitrophenyl β-hydroxyethyl sulphides (BENNETT and BERRY), 1667.
$C_8H_9O_4NS$ Nitrobenzylmethylsulphones (C. K. and E. H. INGOLD and SHAW), 820.
$C_8H_9O_4N_2As$ Hydroxy-1:4-dihydroquinoxaline-6-arsinic acids (EWINS, NEWBERY, and STICKINGS), 853.
$C_7H_9O_5NS$ Methyl nitrobenzylsulphonates (C. K. and E. H. INGOLD and SHAW), 829.
$C_8H_{10}ON_2S$ 3-Aminomethylthiolbenzaldoximes (HODGSON and BEARD), 2427.
Anisylthiocarbamides (DYSON, GEORGE, and HUNTER), 440.
$C_8H_{10}O_4N_2S$ Nitrobenzylsulphonmethylamides (C. K. and E. H. INGOLD and SHAW), 824.
$C_8H_{10}O_4N_2Hg$ Ethyl 1-acetoxymercuriglyoxalinecarboxylate (BALABAN and KING), 1870.
$C_8H_{10}O_6N_2As$ 3-Nitrophenylarsinic acid 4-glycineamide (EWINS, NEWBERY, and STICKINGS), 854.
$C_8H_{11}O_2N_2Cl$ Nitro-β-phenylethylammonium chlorides (GOSS, HANHART, and INGOLD), 253.
$C_8H_{11}O_4N_2As$ Nitrosoethylaminophenylarsinic acid (BURTON and GIBSON), 2387.
$C_8H_{12}O_3NAs$ *o*-Ethylaminophenylarsinic acid (BURTON and GIBSON), 2387.
$C_8H_{15}OBrS$ Tetrahydrothiophen-δ-bromobutylsulphonium bromide, and its picrate (BENNETT and HOCK), 483.
$C_8H_{15}O_2NBr_2$ 4-Bromoacetoxy-1-methylpiperidine (MILLS, PARKIN, and WARD), 2625.
$C_8H_{16}O_3NBr$ 4-Hydroxypiperidylacetic acid methobromides (MILLS, PARKIN, and WARD), 2623.
$C_8H_{17}OBrS$ Tetrahydrothiophen-δ-hydroxybutylsulphonium bromide, and its salts (BENNETT and HOCK), 482.

8 V

$C_8H_6ONClBr_2$ Chlorodibromoacetanilide (SMITH), 1101.
C_8H_6ONClS Chloromethylthiolbenzaldoximes (HODGSON and BEARD), 2427.
$C_8H_6ON_2Br_2S$ 1-Amino-5-methoxybenzthiazole dibromide (DYSON, HUNTER, and MORRIS), 1191.
$C_8H_8O_3NClS$ Nitrophenyl β-chloroethyl sulphides (BENNETT and BERRY), 1672.
$C_8H_8O_3NBrS$ Nitrophenyl β-bromoethyl sulphides (BENNETT and BERRY), 1672.

$C_8H_8O_2NIS$ Nitrophenyl β-iodoethyl sulphides (BENNETT and BERRY), 1673.
$C_8H_8O_3NClS$ Nitrophenyl β-chloroethyl sulphoxides (BENNETT and BERRY), 1672.
$C_8H_8O_3NBrS$ Nitrophenyl β-bromoethyl sulphoxides (BENNETT and BERRY), 1672.

C_9 Group.

$C_9H_6O_4$ 4:5-Methylenedioxyphthalide (STEVENS and ROBERTSON), 2792.
$C_9H_6O_6$ Hydrastic acid, synthesis of (STEVENS and ROBERTSON), 2790.
$C_9H_8O_2$ Cinnamic acid, condensation of, with pyrogallol and resorcinol (ELLISON), 1720.
$C_9H_8O_3$ Acetophenone-*o*-carboxylic acid (DAVIES and POOLE), 2662.
$C_9H_8O_4$ 5-Carboxy-2-hydroxyacetophenone (CHATTAWAY and PRATS), 692.
$C_9H_8O_5$ 6-Hydroxymethylpiperonylic acid, and its silver salt (STEVENS and ROBERTSON), 2792.
$C_9H_{10}O_2$ 1:2-Dihydroxyallylbenzenes (PERKIN and TRIKOJUS), 1665.
$C_9H_{10}O_3$ *m*-Xylorcylaldehyde (ROBERTSON and ROBINSON), 2202.
$C_9H_{10}O_5$ 3:6-Dihydroxy-2:4-dimethoxybenzaldehyde (CHAPMAN, PERKIN, and ROBINSON), 3029.
$C_9H_{11}Br$ β-Tolylethyl bromides, isomeric, preparation and hydrolysis of (SHOESMITH and CONNOR), 1768.
$C_9H_{12}O_2$ β-Methoxyphenylethyl alcohols (SHOESMITH and CONNOR), 2233.
$C_9H_{12}O_4$ *cyclo*Pentane*spiro*paraconic acid, and its silver salt (SIRCAR), 1258.
$C_9H_{12}O_6$ β-Hydroxy-β-ethylbutane-γδδ-tricarboxylic γ-lactone (SIRCAR), 1258.
$C_9H_{13}N$ Trimethylbenzylamine, picrate of (GOSS, HANHART, and INGOLD), 257.
$C_9H_{14}O_2$ ββ-Dipropylacrylic acid, and its silver salt (KON and MAY), 1552.
α-Ethyl-Δ^1-*cyclo*pentenylacetic acid, and its silver salt (KON and NARAYANAN), 1543.
α-Ethyl*cyclo*pentylideneacetic acid (KON and NARAYANAN), 1543.
*cyclo*Heptylideneacetic acid (KON and MAY), 1554.
$C_9H_{14}O_3$ Methyl 2:2-dimethyl*cyclo*pentan-3-one-1-carboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3012.
$C_9H_{14}O_4$ *apo*Fenchocamphoric acid, synthesis of (SHORT), 961.
$C_9H_{14}O_5$ γ-Acetyl-γ-methylbutane-αβ-dicarboxylic acid (BHAGVAT and SIMONSEN), 87.
α-Keto-ββγγ-tetramethylglutaric hydroxylactone (ROTHSTEIN and SHOPPEE), 533.
$C_9H_{14}O_6$ γ-Mannonolactone-acetone (GOODYEAR and HAWORTH), 3143.
$C_9H_{14}N_2$ Aminobenzyldimethylamines, and their hydrochlorides (STEDMAN), 1905.
$C_9H_{16}O_2$ β-Propylhexoic acid (KON and MAY), 1554.
$C_9H_{16}O_3$ 1-Hydroxy-α-ethyl*cyclo*pentaneacetic acid, and its silver salt (KON and NARAYANAN), 1543.

9 III

$C_9H_3N_3S$ 2:5-Dicyanophenylthiocarbimide (DYSON, GEORGE, and HUNTER), 443.
$C_9H_6O_4Cl_2$ ωω-Dichloro-5-carboxy-2-hydroxyacetophenone (CHATTAWAY and PRATS), 691.
$C_9H_7O_2N$ Homophthalimide (SIRCAR), 1255.
$C_9H_8O_5N_2$ β-*O*-Methyl-6-nitro-3:4-methylenedioxybenzaldoxime (BRADY and KLEIN), 894.
$C_9H_8O_7N_2$ Methyl 2:3-dinitro-4-methoxybenzoate (DADSWELL and KENNER), 587.
$C_9H_9O_3Cl$ Chlorotropic acids (KERR), 1947.
$C_9H_9O_6N$ 3-Nitro-2:4-dimethoxybenzoic acid (DADSWELL and KENNER), 587.

$C_9H_9NO_3$ *m*-Methoxy-ω-nitrostyrene (SHOESMITH and CONNOR), 2232.
C_9H_9NS Xylylthiocarbimides (DYSON, GEORGE, and HUNTER), 440.
$C_9H_{10}OBr_2$ β-Bromo-2-methoxyphenylethylbromides (SHOESMITH and CONNOR), 2233.
$C_9H_{10}O_2Se$ *o*-Tolylselenoglycollic acid (PORRITT), 28.
$C_9H_{10}O_4N_2$ Methyl *p*-nitrobenzylaminoformate (BAKER), 568.
$C_9H_{10}O_6N_2$ Dinitrohomoveratroles (OXFORD), 1968.
$C_9H_{10}N_2S$ *p*-Dimethylaminophenylthiocarbimide (DYSON, GEORGE, and HUNTER), 442.
$C_9H_{11}ON_3$ 2:3-Dicyano-1-methyl-1-ethyl*cyclo*propane-2-carboxylamide (SIRCAR), 1258.
$C_9H_{11}OBr$ β-*p*-Methoxyphenylethyl bromide (SHOESMITH and CONNOR), 2234.
$C_9H_{11}OI$ Benzyl β-iodoethyl ether (BENNETT and HOCK), 476.
$C_9H_{11}O_2N$ *m*-Methoxyphenylacetaldoxime (SHOESMITH and CONNOR), 2232.
$C_9H_{11}O_3N$ α-Amino-β-hydroxy-α-phenylpropionic acid, and its hydrochloride (KERR), 1946.
$C_9H_{11}O_4N$ 5-Nitro-2:4-dimethoxytoluene (DADSWELL and KENNER), 585.
$C_9H_{11}ClS$ Phenyl γ-chloropropyl sulphide (BENNETT and BERRY), 1680.
$C_9H_{12}ON_4$ Acetophenone-δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 109.
$C_9H_{12}O_2N_2$ Nitrobenzyldimethylamines, and their hydrochlorides (STEDMAN), 1904.
α-*p*-Nitrophenyl*iso*propylamine, picrate of (BAKER and INGOLD), 264.
$C_9H_{13}O_3Br_2$ Methyl 4:4-dibromo-2:2-dimethyl*cyclo*pentan-3-one-1-carboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3012.
$C_9H_{12}O_3S$ α-Phenylpropanesulphonic acid, and its resolution and salts (EVANS, MABBOTT, and TURNER), 1165.
$C_9H_{13}N_2S$ Xylylthiocarbamides (DYSON, GEORGE, and HUNTER), 440.
$C_9H_{13}ON$ Hydroxybenzyldimethylamines, and their salts (STEDMAN), 1904.
$C_9H_{13}O_2N$ *trans*-Hexahydrohomophthalimide (SIRCAR), 1255.
*cyclo*Hexane*spiro*succinimide (SIRCAR), 1254.
*cyclo*Pentanediacetimide (SIRCAR), 604.
$C_9H_{13}N_2S$ *p*-Dimethylaminophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 442.
δ-α-Phenylethylthiosemicarbazide, and its hydrochloride (BAIRD, BURNS, and WILSON), 2532.
$C_9H_{15}ON$ α-Ethyl-Δ¹-*cyclo*pentenylacetamide (KON and NARAYANAN), 1543.
α-Ethyl*cyclo*pentylideneacetamide (KON and NARAYANAN), 1543.
β-Propyl-Δβ-hexeno-amide (KON and MAY), 1553.
$C_9H_{15}O_2N$ ββ-Diethylglutarimide (SIRCAR), 604.
$C_9H_{18}ON_4$ Di(methylethyl ketone) carbohydrazone (BROWN, PICKERING, and WILSON), 109.

9 IV

C_9H_7ONS *p*-Acetylphenylthiocarbimide (DYSON, GEORGE, and HUNTER), 442.
$C_9H_8O_2N_2Cl_2$ Methyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.
$C_9H_8O_2N_2Br_2$ Methyl glyoxylate 2:4-dibromophenylhydrazone (CHATTAWAY and BENNETT), 2851.
$C_9H_8O_3N_2S$ 2-Nitro-4-ethoxyphenylthiocarbimide (DYSON, GEORGE, and HUNTER), 444.
C_9H_9ONS Ethoxyphenylthiocarbimides (DYSON, GEORGE, and HUNTER), 441.
4-Ketotetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2750.
$C_9H_9O_2NS$ Dimethoxyphenylthiocarbimides (DYSON, GEORGE, and HUNTER), 441.

$C_9H_9O_4NS$ *o*-Nitrophenylthiolpropionic acid (MILLS and WHITWORTH), 2750.
$C_9H_9N_2ClS$ 5-Chloro-1-dimethylaminobenzthiazole (HUNTER and STYLES), 1213.
$C_9H_{10}ONCl$ 2-Chloroaceto-*p*-toluidide, dimorphism of (SCHOFIELD), 2903.
$C_9H_{10}ON_2S$ *p*-Acetylphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 442.
1-Amino-5-ethoxybenzthiazole (DYSON, HUNTER, and MORRIS), 1191.
$C_9H_{10}O_2NBr$ 6-Bromo-β-piperonylethylamine, and its salts (STEVENS), 184.
$C_9H_{10}O_2N_3Cl$ Chloromethoxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 1741, 3042.
$C_9H_{10}O_2N_3Br$ Bromomethoxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 3042.
$C_9H_{10}O_2N_3I$ Iodomethoxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 3043.
$C_9H_{10}O_3NBr$ α-6-Bromo-3:4-dimethoxybenzaldoxime, sulphate of (BRADY and WHITEHEAD), 2936.
$C_9H_{10}O_4NBr$ 6-Bromo-2-nitrohomoveratrole (OXFORD), 1970.
$C_9H_{10}N_2Br_2S$ 1-Dimethylaminobenzthiazole dibromide (HUNTER and STYLES), 1211.
$C_9H_{10}N_2Br_6S$ 1-Dimethylaminobenzthiazole hexabromide (HUNTER and STYLES), 1212.
$C_9H_{11}O_2NS$ *o*-Aminophenylthiolpropionic acid (MILLS and WHITWORTH), 2750.
$C_9H_{11}O_2ClS$ α-Phenylpropanesulphonyl chloride (EVANS, MABBOTT, and TURNER), 1166.
$C_9H_{11}O_3NS$ *p*-Nitrobenzyl β-hydroxyethyl sulphide (BENNETT and BERRY), 1671.
p-Nitrophenyl γ-hydroxypropyl sulphide (BENNETT and BERRY), 1671.
$C_9H_{11}O_3N_3S$ 2-Nitro-4-ethoxyphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.
$C_9H_{11}N_2ClS$ *s*-*p*-Chlorophenyldimethylthiocarbamide (HUNTER and STYLES), 1213.
$C_9H_{11}N_2Br_5S$ 1-Dimethylaminobenzthiazole tetrabromide hydrobromide (HUNTER and STYLES), 1211.
$C_9H_{12}ON_2S$ Ethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.
$C_9H_{12}O_2N_2S$ Dimethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.
$C_9H_{12}O_4N_2S$ Nitrobenzylsulphondimethylamides (C. K. and E. H. INGOLD, and SHAW), 826.
Nitrobenzylsulphonethylamides (C. K. and E. H. INGOLD, and SHAW), 825.
$C_9H_{13}O_2NS$ Benzylsulphonethylamide (C. K. and E. H. INGOLD, and SHAW), 818.
$C_9H_{13}O_2N_2Cl$ γ-*p*-Nitrophenylpropylammonium chloride (INGOLD and WILSON), 813.
$C_9H_{14}O_2N_2S$ Ethyl 2-ethylthiolmethylglyoxalinecarboxylate, and its salts (BALABAN and KING), 1866.

9 V

$C_9H_7ON_2ClS$ 5-Chloro-1-acetylaminobenzthiazole (DYSON, HUNTER, and MORRIS), 1190.
$C_9H_{10}O_3NClS$ *p*-Nitrophenyl γ-chloropropyl sulphide (BENNETT and BERRY), 1672.
$C_9H_{10}N_2ClBr_3S$ 5-Chloro-1-dimethylaminobenzthiazole dibromide hydrobromide (HUNTER and STYLES), 1213.
$C_9H_{11}ON_2Br_5S$ 1-Amino-5-ethoxybenzthiazole tetrabromide hydrobromide (DYSON, HUNTER, and MORRIS), 1191.

9 VI

$C_9H_7ON_2ClBr_4S$ 5-Chloro-1-acetamidobenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1191.

C_{10} Group.

$C_{10}H_{16}$ Pinene, recovery of, from its nitroso-chloride (EARL and KENNER), 1269.

10 II

$C_{10}H_8O_3$ 4-Hydroxy-3-methylcoumarin (HEILBRON and HILL), 1706.
4-Methoxycoumarin (HEILBRON and HILL), 1707.
$C_{10}H_8O_4$ 6-Hydroxymethylhomopiperonylolactone (STEVENS), 181.
$C_{10}H_{10}O_2$ Methyl atropate (BAKER and ECCLES), 2129.
Safrole, synthesis of (PERKIN and TRIKOJUS), 1663.
$C_{10}H_{10}O_4$ *m*-Methoxyphenylpyruvic acid (CHAKRAVARTI, HAWORTH, and PERKIN), 2270.
$C_{10}H_{10}N_2$ 2:3-Dimethyl-1:2:3:4-tetrahydroquinoxalines, stereoisomeric, and their tartrates (GIBSON), 342.
$C_{10}H_{12}O_2$ Ethyl phenylacetate, nitration of (BAKER and INGOLD), 834.
$C_{10}H_{12}O_3$ 2:4-Dimethoxymethylbenzaldehydes (ROBERTSON and ROBINSON), 2200.
$C_{10}H_{12}O_5$ Antiarolaldehyde (CHAPMAN, PERKIN, and ROBINSON), 3029.
n-Propyl gallate (CLARKE, ROBINSON, and SMITH), 2649.
Substance, from acetylation of antiarol (CHAPMAN, PERKIN, and ROBINSON), 3033.
Substance, from oxidation of 4:4:5-trimethyl-Δ^5-*cyclo*pentene-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 86.
$C_{10}H_{13}Br$ α-Phenylbutyl bromide (EVANS, MABBOTT, and TURNER), 1166.
$C_{10}H_{14}O_2$ Benzyl γ-hydroxypropyl ether (BENNETT and HOCK), 474.
$C_{10}H_{14}O_3$ Camphorquinone, action of sulphuric acid on (BHAGVAT and SIMONSEN), 77.
$C_{10}H_{14}O_4$ $\alpha\zeta$-Diacetoxy-$\Delta^{\beta\delta}$-hexadiene (FARMER, LAROIA, SWITZ, and THORPE), 2950.
4-Hydroxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylic acid (BHAGVAT and SIMONSEN), 83.
4:4:5-Trimethyl-Δ^5-*cyclo*pentene-1:3-dicarboxylic acids (BHAGVAT and SIMONSEN), 84.
$C_{10}H_{14}O_8$ $\beta\gamma$-Dimethylbutane-$\alpha\alpha\beta\delta$-tetracarboxylic acids (VOGEL), 1990.
$C_{10}H_{16}O$ Pulegones (HUGH, KON, and LINSTEAD), 2585.
$C_{10}H_{16}O_3$ Tetramethyladipic anhydrides (FARMER and KRACOVSKI), 683.
$C_{10}H_{16}O_4$ 4:4:5-Trimethyl*cyclo*pentane-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 85.
$C_{10}H_{16}O_5$ 1-Hydroxy-4:4:5-trimethyl*cyclo*pentane-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 84.
$C_{10}H_{18}O_3$ 1-Hydroxy-α-ethyl*cyclo*hexaneacetic acid, and its silver salt (KON and NARAYANAN), 1539.
$C_{10}H_{18}O_6$ Tetramethyl gluconolactones (DREW, GOODYEAR, and HAWORTH), 1241; oxidation of (HAWORTH, HIRST, and MILLER), 2436.
Tetramethyl mannonolactone (DREW, GOODYEAR, and HAWORTH), 1243.
$C_{10}H_{18}O_7$ Substance, from oxidation of tetramethyl γ-fructose (HAWORTH, HIRST, and NICHOLSON), 1520.
$C_{10}H_{20}O_3$ β-Hydroxy-β-methyl-α-ethylpentanoic acid, and its silver salt (KON and NARAYANAN), 1544.
$C_{10}H_{20}O_6$ Tetramethylglucose, mutarotation of, in aqueous alcohols (RICHARDS, FAULKNER, and LOWRY), 1733.
Tetramethylglucoses, structure of (HAWORTH, HIRST, and MILLER), 2436.
2:3:4:6-Tetramethylmannose (DREW, GOODYEAR, and HAWORTH), 1243.
$C_{10}H_{21}N$ *d-neoiso*Menthylamine, and its salts (READ and ROBERTSON), 2172.
$C_{10}H_{22}O_2$ $\alpha\zeta$-Diethoxyhexane (FARMER, LAROIA, SWITZ, and THORPE), 2951.
$C_{10}H_{24}N_2$ *s*-Tetramethyldiethylethylenediamine, dipicrate of (HANHART and INGOLD), 1011.

10 III

$C_{10}H_6O_2Cl_2$ 1:8-Naphthalyl chloride, preparation and reactions of (DAVIES and LEEPER), 1124.

$C_{10}H_8O_2S$ 1:8-Thionyldihydroxynaphthalene (GREEN), 2344.
$C_{10}H_7O_2N$ Cyanocinnamic acids (DAVIES and POOLE), 2661.
$C_{10}H_7O_2Br_5$ Pentabromosafrole (PERKIN and TRIKOJUS), 1666.
$C_{10}H_7O_4N_3$ 1-Phenyl-4-oximino-5-ketopyrazoline-3-carboxylic acid (CHATTAWAY and HUMPHREY), 2137.
$C_{10}H_8O_3S$ Methyl benzylsulphonate (C. K. and E. H. INGOLD and SHAW), 819.
$C_{10}H_8O_7N_2$ Ethyl 2:4-dinitrobenzoylformate (FAIRBOURNE and FAWSON), 49.
$C_{10}H_9O_2N$ Nitrosodihydro-α-naphthols (ROWE and LEVIN), 531.
$C_{10}H_9O_3N_3$ 1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid, and its hydrochloride (CHATTAWAY and HUMPHREY), 2135.
$C_{10}H_9O_4N$ Methyl *p*-nitroatropate (BAKER and ECCLES), 2131.
Nitrobenzoylacetones (BURGESS), 2018.
6-Nitro*iso*safrole (ROBINSON and ZAKI), 2489.
$C_{10}H_9O_4Br$ 6-Bromomethylhomopiperonylic acid (STEVENS), 186.
$C_{10}H_9O_6N$ *m*-Nitrobenzylmalonic acid (BAKER and ECCLES), 2127.
$C_{10}H_{10}O_{10}Hg$ Mercuretin (MARSH and STRUTHERS), 2658.
$C_{10}H_{11}ON_3$ *cyclo*Pentane*spiro*-2:3-dicyano*cyclo*propane-2-carboxylamide (SIRCAR), 1258.
$C_{10}H_{11}O_2N$ 6-Amino*iso*safrole, and its hydrochloride (ROBINSON and ZAKI), 2490.
5:6-Dimethoxyindole (OXFORD and RAPER), 420.
2:6-Dimethoxy-4-methylbenzonitrile (ROBERTSON and ROBINSON), 2201.
$C_{10}H_{11}O_3N$ Acetopiperonylmethylamide (MALAN and ROBINSON), 2655.
4-Nitro-*ar*-tetrahydro-α-naphthol (ROWE and LEVIN), 531.
$C_{10}H_{11}O_3Cl$ Acetylchlorocreosol (OXFORD), 1966.
$C_{10}H_{11}O_4N$ 6-Hydroxymethylhomopiperonylamide (STEVENS), 182.
$C_{10}H_{11}O_4N_3$ *m*-Nitrobenzylmalonamide (BAKER and ECCLES), 2127.
$C_{10}H_{11}O_6N$ Methyl 3-nitro-2:4-dimethoxybenzoate (DADSWELL and KENNER), 587.
2-Nitro-4:5-dimethoxyphenylacetic acid (OXFORD and RAPER), 419.
$C_{10}H_{12}O_2Se$ Xylyl-4-selenoglycollic acids (PORRITT), 28.
$C_{10}H_{12}O_4N_2$ Acetylnitro-4-methoxytoluidines (DADSWELL and KENNER), 584.
Methyl benzylmethylaminoformate (BAKER), 570.
$C_{10}H_{12}N_2S$ 1-Dimethylaminomethylbenzthiazoles (HUNTER and STYLES), 1212.
$C_{10}H_{13}ON$ Acetoxylidides, and their salts (DADSWELL and KENNER), 1104.
$C_{10}H_{13}OCl$ Benzyl γ-chloropropyl ether (BENNETT and HOCK), 474.
$C_{10}H_{13}O_2N$ Methyl benzylmethylaminoformate (BAKER), 567.
$C_{10}H_{13}O_3N$ 3:5-Dimethoxyacetanilide (OAKESHOTT and PLANT), 489.
2:6-Dimethoxy-4-methylbenzamide (ROBERTSON and ROBINSON), 2200.
$C_{10}H_{13}O_5N$ Oxime from substance $C_{10}H_{12}O_5$ (BHAGVAT and SIMONSEN), 86.
$C_{10}H_{13}N_3S$ Benzaldehyde *S*-ethylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2529.
$C_{10}H_{14}O_2N_2$ Dimethylnitro-β-phenylethylamines, salts of (GOSS, HANHART, and INGOLD), 255.
Nitrobenzyltrimethylamines, picrates of (GOSS, HANHART, and INGOLD), 260.
$C_{10}H_{14}O_3S$ α-Phenylbutanesulphonic acid, sodium salt (EVANS, MABBOTT, and TURNER), 1166.
$C_{10}H_{14}N_2S$ *s*-Tolyldimethylthiocarbamides (HUNTER and STYLES), 1212.
$C_{10}H_{15}ON$ Methoxybenzyldimethylamines, and their hydrochlorides (STEDMAN), 1904.
$C_{10}H_{15}O_2N$ β-2:3-Dimethoxyphenylethylamine, and its salts (HAWORTH), 2283.
*cyclo*Hexanediacetimide (SIRCAR), 604.

$C_{10}H_{15}O_5Cl$ Trihydroxymethoxyflavylium chlorides (ROBERTSON and ROBINSON), 1715.

$C_{10}H_{16}O_4N_6$ 2:2-Dimethyl*cyclo*pentane-3:4-dione-1-carboxylic acid disemicarbazone (GIBSON, HARIHARAN, and SIMONSEN), 3014.

$C_{10}H_{17}ON$ α-Ethyl-Δ^1-*cyclo*hexenylacetamide (KON and NARAYANAN), 1540.

$C_{10}H_{18}O_4S$ Ethyl thiodipropionate (BENNETT and SCORAH), 196.

$C_{10}H_{19}ON_3$ δ-Methyl-γ-ethyl-Δ^δ-hexen-β-one semicarbazone (KON and NARAYANAN), 1545.

$C_{10}H_{19}O_6N$ Substance, from oxidation of tetramethyl γ-fructose (HAWORTH, HIRST, and NICHOLSON), 1521.

$C_{10}H_{20}O_5N_2$ *l*-Arabotrimethoxyglutaromethylamide (HAWORTH and JONES), 2353.
i-Trimethoxyglutaromethylamide (HAWORTH and JONES), 2352.

$C_{10}H_{26}N_2I_2$ *s*-Tetramethyldiethylethylenediammonium di-iodide (HANHART and INGOLD), 1011.

10 IV

$C_{10}H_4O_6N_2Cl_6$ Anhydro-3:5-dinitro-2βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY and MORRIS), 2015.

$C_{10}H_5O_4Cl_7S$ Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene-5-sulphonyl chloride (CHATTAWAY and MORRIS), 2016.

$C_{10}H_6ONCl$ *o*-Cyano*allo*cinnamyl chloride (DAVIES and POOLE), 2663.

$C_{10}H_6O_5Cl_6S$ Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene-5-sulphonic acid, and its ammonium salt (CHATTAWAY and MORRIS), 2014.

$C_{10}H_8O_3NCl$ 6-Chloromethylhomopiperonylonitrile (STEVENS), 182.

$C_{10}H_8O_6N_2Cl_2$ ωω-Dichloro-3:5-dinitro-2-ethoxyacetophenone (CHATTAWAY and MORRIS), 2016.

$C_{10}H_9O_2NS$ Carbethoxyphenylthiocarbimides (DYSON, GEORGE, and HUNTER), 441.

$C_{10}H_9O_3NS$ 3-Keto-2:3-dihydro-1:4-benzthiazine-2-acetic acid (MILLS and WHITWORTH), 2751.

$C_{10}H_{10}O_3N_2Cl_2$ Ethyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.

$C_{10}H_{10}O_2N_2Br_2$ Ethyl glyoxylate 2:4-dibromophenylhydrazone (CHATTAWAY and BENNETT), 2852.

$C_{10}H_{10}O_2N_2S$ 1-Amino-5-carbethoxybenzthiazole (DYSON, HUNTER, and MORRIS), 1190.

$C_{10}H_{10}O_3NCl$ Ethyl β-4-hydroxypiperidylacetate methochloride (MILLS, PARKIN, and WARD), 2624.

$C_{10}H_{11}ONS$ 4-Keto-2-methyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2749.

$C_{10}H_{12}ONCl$ Chloroaceto-*m*-2-xylidides (DADSWELL and KENNER), 1106.

$C_{10}H_{12}ONI$ 1-Methylbenzoxazole ethiodide (HAMER), 2803.

$C_{10}H_{12}ON_2S$ 1-Dimethylamino-5-methoxybenzthiazole (HUNTER and STYLES), 1212.

$C_{10}H_{12}O_3NBr$ Methylbromopiperonylethylamine, and its salts (STEVENS), 185.

$C_{10}H_{12}O_2N_2S$ Carbethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.

$C_{10}H_{13}N_2Br_4S$ 1-Dimethylamino-3-methylbenzthiazole tetrabromide (HUNTER and STYLES), 1212.

$C_{10}H_{12}N_2Br_6S$ 1-Dimethylamino-5-methylbenzthiazole hexabromide (HUNTER and STYLES), 1213.

$C_{10}H_{13}N_2Br_5S$ 1-Dimethylamino-5-methylbenzthiazole tetrabromide hydrobromide (HUNTER and STYLES), 1212.

$C_{10}H_{14}ON_2S$ *s*-*p*-Methoxyphenyldimethylthiocarbamide (HUNTER and STYLES), 1212.

$C_{10}H_{15}O_2N_2I$ *p*-Nitrobenzyltrimethylammonium iodide (STEDMAN), 1905.

$C_{10}H_{15}O_5N_2As$ 3-Nitro-6-diethylaminophenylarsinic acid (BURTON and GIBSON), 2388.

$C_{10}H_{20}O_3NBr$ Ethyl 4-hydroxy-1-piperidylacetate methobromides (MILLS, PARKIN, and WARD), 2622.

10 V

$C_{10}H_5O_4NCl_8S$ Anhydro-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\delta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphondichloroamide (CHATTAWAY and MORRIS), 2017.

$C_{10}H_7O_4NCl_6S$ Anhydro-2-$\delta\beta\delta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphonamide (CHATTAWAY and MORRIS), 2017.

$C_{10}H_{10}O_2N_2ClBr$ Ethyl glyoxylate chlorobromophenylhydrazones (CHATTAWAY and BENNETT), 2852.

$C_{10}H_{10}O_2N_2Br_2S$ 1-Amino-5-carbethoxybenzthiazole dibromide (DYSON, HUNTER, and MORRIS), 1190.

$C_{10}H_{12}ON_2Cl_5Mo$ Dipyridinium molybdenyl pentachloride (JAMES and WARDLAW), 2148.

$C_{10}H_{12}ON_2Br_4S$ 1-Dimethylamino-5-methoxybenzthiazole tetrabromide (HUNTER and STYLES), 1212.

$C_{10}H_{13}O_2N_2Cl_7As$ 3-Nitro-6-diethylaminophenylarsenious chloride (BURTON and GIBSON), 2388.

C_{11} Group.

$C_{11}H_8Br_2$ 5-Bromo-α-naphthylmethyl bromide (SHOESMITH and RUBLI), 3104.

$C_{11}H_{10}O_3$ 4-Methoxy-3-methylcoumarin (HEILBRON and HILL), 1707.

$C_{11}H_{10}O_5$ 3:4-Dimethoxyhomophthalic anhydride (HAWORTH, KOEPFLI, and PERKIN), 551.

$C_{11}H_{10}O_6$ *O*-Diacetylphloroglucinaldehyde (ROBERTSON and ROBINSON), 1712.

$C_{11}H_{12}O_5$ 6-Methoxymethylhomopiperonylic acid, and its silver salt (STEVENS), 185.

5-Methylcarbonato-orcylaldehyde 3-methyl ether (HIRST), 2495.

$C_{11}H_{12}N_2$ 8-Amino-2:4-dimethylquinoline (ROBERTS and TURNER), 1856.

$C_{11}H_{14}O_3$ Ethyl *m*-tolyloxyacetate (SMITH), 176.

Propylvanillins (DICKINSON, HEILBRON, and IRVING), 1895.

$C_{11}H_{14}O_5$ *O*-Acetylantiarol (CHAPMAN, PERKIN, and ROBINSON), 3029.

$C_{11}H_{14}O_6$ ω-5:6-Trimethoxyresacetophenone (CHAPMAN, PERKIN, and ROBINSON) 3033.

$C_{11}H_{16}O_2$ Benzyl δ-hydroxybutyl ether (BENNETT and HOCK), 475.

4-*n*-Butoxyanisole (CLARKE, ROBINSON, and SMITH), 2651.

$C_{11}H_{16}O_4$ Methyl 4-hydroxy-2:2:3-trimethyl-Δ^3-cyclohexen-5-one-1-carboxylate (BHAGVAT and SIMONSEN), 82.

$C_{11}H_{16}O_6$ Acetyl-α-keto-$\beta\beta\gamma\gamma$-tetramethylglutaric hydroxylactone (ROTHSTEIN and SHOPPEE), 534.

$C_{11}H_{18}O_2$ $\beta\beta$-Di*iso*butylacrylic acid (KON and MAY), 1554.

$C_{11}H_{18}O_4$ α-Ethyl*cyclo*pentane-1:1-diacetic acid, and its silver salt (KON and NARAYANAN), 1544.

$C_{11}H_{18}O_6$ Dimethyl γ-mannonolactone-acetone (GOODYEAR and HAWORTH), 3142.

$C_{11}H_{20}O_3$ Ethyl-1-hydroxy-α-ethyl*cyclo*pentaneacetate (KON and NARAYANAN), 1543.

$C_{11}H_{20}O_7$ Substance, from oxidation of tetramethylfructose (HAWORTH, HIRST, and LEARNER), 1047; (AVERY, HAWORTH, and HIRST), 2813.

11 III

$C_{11}H_5O_3Cl_7$ Acid chloride of anhydro-5-carboxy-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{11}H_8O_4Cl_6$ Anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 687.
$C_{11}H_7NCl_4$ Tetrachloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1848.
$C_{11}H_8O_4N_2$ Anhydrodiketosuccinic acid tolylhydrazones (CHATTAWAY and HUMPHREY), 2794.
$C_{11}H_8O_8N_4$ Ethyl 2:4:6-trinitrophenylcyanoacetate (FAIRBOURNE and FAWSON) 48.
$C_{11}H_8NCl_3$ Trichloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1852.
$C_{11}H_9OBr$ 5-Bromo-α-naphthylcarbinol (SHOESMITH and RUBLI), 3104.
4-Bromo-α-naphthyl methyl ether (SHOESMITH and RUBLI), 3102.
$C_{11}H_9O_5Br$ 6-Bromo-3:4-dimethoxyhomophthalic anhydride (HAWORTH, KOEPFLI, and PERKIN), 551.
$C_{11}H_9O_6N_3$ Ethyl 2:4-dinitrophenylcyanoacetate, and its sodium salt (FAIRBOURNE and FAWSON), 47.
$C_{11}H_9NCl_2$ Dichloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1846.
$C_{11}H_{10}ON_2$ 3-Keto-3:4:5:6-tetrahydro-4-carboline (MANSKE and ROBINSON), 242.
$C_{11}H_{10}O_2N_2$ 8-Nitro-2:4-dimethylquinoline (ROBERTS and TURNER), 1856.
$C_{11}H_{10}O_5N_2$ Diketosuccinic acid tolylhydrazones (CHATTAWAY and HUMPHREY), 2794.
$C_{11}H_{10}NCl$ Chloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1845.
$C_{11}H_{10}NBr$ 4-Bromo-2-methyl-α-naphthylamine (SHOESMITH and RUBLI), 3103.
$C_{11}H_{10}N_2Cl_2$ Dichloroamino-2:4-dimethylquinolines (ROBERTS and TURNER), 1850.
$C_{11}H_{11}O_3Br$ 4-Bromo-6:7-dimethoxy-1-hydrindone (HAWORTH, KOEPFLI, and PERKIN), 550.
$C_{11}H_{11}O_4N$ 5:6-Dimethoxyindole-2-carboxylic acid (OXFORD and ROPER), 420.
$C_{11}H_{11}O_4Cl_3$ 5-Carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.
$C_{11}H_{11}O_4Br$ Methyl 6-bromomethylhomopiperonylate (STEVENS), 186.
$C_{11}H_{11}O_6Br$ 6-Bromo-3:4-dimethoxyhomophthalic acid (HAWORTH, KOEPFLI, and PERKIN), 551.
$C_{11}H_{11}N_2Cl$ Chloroamino-2:4-dimethylquinolines (ROBERTS and TURNER), 1848.
$C_{11}H_{13}ON$ γ-Benzyloxybutyronitrile (BENNETT and HOCK), 474.
$C_{11}H_{13}ON_3$ β-3-Indolylpropionhydrazide (MANSKE and ROBINSON), 241.
$C_{11}H_{13}O_4Br$ β-6-Bromoveratrylpropionic acid (HAWORTH, KOEPFLI, and PERKIN), 550.
$C_{11}H_{13}N_3S$ Benzaldehyde *S*-allylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2530.
$C_{11}H_{15}ON_3$ *meso*-1-Carbamyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 345.
$C_{11}H_{15}OCl$ Benzyl chlorobutyl ether (BENNETT and HOCK), 476.
$C_{11}H_{15}O_3N$ β-2:3-Dimethoxyphenylpropionamide (HAWORTH), 2282.
$C_{11}H_{15}O_4N$ Nitro-4-*n*-butoxyanisole (CLARKE, ROBINSON, and SMITH), 2649.
$C_{11}H_{15}O_5N_3$ Antiarolaldehyde semicarbazone (CHAPMAN, PERKIN, and ROBINSON), 3030.
Semicarbazone from substance $C_{10}H_{12}O_5$ (BHAGVAT and SIMONSEN), 86.
$C_{11}H_{15}N_3S$ Acetone δ-benzylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2530.
Benzaldehyde *S*-propylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2529.
$C_{11}H_{16}ON_2$ Methyl ethyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2115.
$C_{11}H_{16}O_2N_2$ Trimethylnitro-β-phenylethylamines, salts of (GOSS, HANHART, and INGOLD), 257.

$C_{11}H_{16}O_3Br$ Methyl 5:5-dibromo-2:2:3-trimethyl*cyclo*hexan-4-one-1-carboxylate (BHAGVAT and SIMONSEN), 82.

$C_{11}H_{17}ON$ Methylephedrines, and their salts (SMITH), 2057.

$C_{11}H_{17}O_4N$ Methyl 5-oximino-2:2:3-trimethyl*cyclo*hexan-4-one-1-carboxylate (BHAGVAT and SIMONSEN), 87.

$C_{11}H_{18}O_4N_2$ Methyl 4-hydroxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-ζ-one-1-carboxylate dioxime (BHAGVAT and SIMONSEN), 82.

$C_{11}H_{21}ON_3$ δ-*d*-Bornylsemicarbazides, and their hydrochlorides (GOODSON), 1998.

$C_{11}H_{22}O_2N_2$ *n*-Nonanedicarboxyamide (BARNICOAT), 2928.

$C_{11}H_{23}N_3S$ Acetone δ-heptylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2533.

11 IV

$C_{11}H_5O_3NCl_6$ Anhydro-5-cyano-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro α-hydroxyethylbenzene (CHATTAWAY and PRATS), 688.

$C_{11}H_7O_3NCl_6$ Amide of anhydro-5-carboxy-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{11}H_7O_8NS_2$ *ON*-Carbonyl-1:8-aminonaphthol-3:6-disulphonic acid, salts (BALABAN and KING), 3091.

$C_{11}H_8O_2N_2Cl_2$ Dichloronitro-2:4-dimethylquinoline (ROBERTS and TURNER), 1847.

$C_{11}H_8O_5Cl_6S$ Methyl anhydro-2-$\beta\beta\beta$-trichloro-α-hydroxyethyl-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphonate (CHATTAWAY and MORRIS), 2017.

$C_{11}H_8O_6N_3Cl$ Ethyl 2:4-dinitrochlorophenylcyanoacetate (FAIRBOURNE and FAWSON), 50.

$C_{11}H_8O_6N_3Br$ Ethyl 2:4-dinitrobromophenylcyanoacetate (FAIRBOURNE and FAWSON), 49.

$C_{11}H_8O_7N_3Br$ Ethyl-2:4-dinitrobromophenylhydroxycyanoacetate (FAIRBOURNE and FAWSON), 50.

$C_{11}H_9O_2N_2Cl$ Chloronitro-2:4-dimethylquinolines (ROBERTS and TURNER), 1848.

$C_{11}H_{10}O_3NCl$ γ-Chloro-α-cyanopropyl benzoate (CRAWFORD and KENYON), 400.

$C_{11}H_{10}O_4NBr$ 6-Bromo-2-carboxy-3:4-dimethoxyphenylacetonitrile (HAWORTH, KOEPFLI, and PERKIN), 551.

4-Bromo-2-*iso*nitroso-6:7-dimethoxy-1-hydrindone (HAWORTH, KOEPFLI, and PERKIN), 550.

$C_{11}H_{11}ONCl_2$ β-Dichloroanilinopropenyl methyl ketones (ROBERTS and TURNER), 1843.

$C_{11}H_{11}O_3NS$ Acetyl-4-ketotetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2750.

$C_{11}H_{11}O_3NS$ 4-Ketotetrahydro-1:5-heptabenzthiazine-2-acetic acids, and their salts (MILLS and WHITWORTH), 2743.

$C_{11}H_{11}O_4N_3Br_2$ 1:3-Dibromo-2:4-dinitro-5-piperidinobenzene (LE FÈVRE and TURNER), 1119.

$C_{11}H_{12}ONCl$ β-Chloroanilinopropenyl methyl ketones (ROBERTS and TURNER), 1842.

$C_{11}H_{12}O_2N_2Cl_2$ 4:5-Dichloro-1-nitro-2-piperidinobenzene (LE FÈVRE and TURNER), 1117.

n-Propyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.

$C_{11}H_{12}O_2N_2Br_2$ *n*-Propyl glyoxylate 2:4-dibromophenylhydrazone (CHATTAWAY and BENNETT), 2852.

$C_{11}H_{12}O_3NBr$ 4-Bromo-6:7-dimethoxy-1-hydrindone oxime (HAWORTH, KOEPFLI, and PERKIN), 550.

$C_{11}H_{12}O_4N_4S$ Penthian-4-one 2:4-dinitrophenylhydrazone (BENNETT and SCORAH), 199.

$C_{11}H_{12}NBrS$ 1-Methylbenzthiazole allobromide (HAMER), 2802.
$C_{11}H_{13}O_2NS$ *o*-Diacetylaminothioanisole (MILLS and WHITWORTH), 2752.
$C_{11}H_{13}O_2N_2Cl$ 2-Chloro-4-nitropiperidinobenzene (LE FÈVRE and TURNER), 1117.
$C_{11}H_{13}O_2N_2Br$ 4-Bromo-2-nitropiperidinobenzene (LE FÈVRE and TURNER), 1117.
$C_{11}H_{14}ON_2S$ 1-Dimethylamino-5-ethoxybenzthiazole (HUNTER and STYLES), 1212.
$C_{11}H_{15}O_2N_3S$ *S*-*o*-Carbethoxybenzylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2530.
$C_{11}H_{15}O_5N_2As$ 3-Nitro-4-piperidinophenylarsinic acid, and its salts (KING), 1053.
$C_{11}H_{16}ON_2S$ *s*-*p*-Ethoxyphenyldimethylthiocarbamide (HUNTER and STYLES), 1212.
$C_{11}H_{16}O_2NI$ Piperonylmethyltrimethylammonium iodide (MALAN and ROBINSON), 2655.
$C_{11}H_{17}O_2NS$ Benzylsulphondiethylamide (C. K. and E. H. INGOLD and SHAW), 819.
$C_{11}H_{17}O_3N_2As$ 3-Amino-4-piperidinophenylarsinic acid, and its salts (KING), 1053.

11 V

$C_{11}H_{14}ON_2Br_4S$ 1-Dimethylamino-5-ethoxybenzthiazole tetrabromide (HUNTER and STYLES), 1212.

C_{12} Group.

$C_{12}H_{20}$ $\beta\epsilon$-Dimethyl-$a\zeta$-diethylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2958.

12 II

$C_{12}H_7Br_3$ 2:4:6-Tribromodiphenyl (BLAKEY and SCARBOROUGH), 3008.
$C_{12}H_8Cl_2$ 2:5-Dichlorodiphenyl (SCARBOROUGH and WATERS), 94.
$C_{12}H_8Br_2$ 2:5-Dibromodiphenyl (SCARBOROUGH and WATERS), 94.
Dibromodiphenyls (BLAKEY and SCARBOROUGH), 3007.
$C_{12}H_{10}O_2$ 3-Methoxy-*a*-naphthaldehyde (SHOESMITH and RUBLI), 3101.
$C_{12}H_{12}N_2$ Harman (MANSKE, PERKIN, and ROBINSON), 11.
$C_{12}H_{11}Br$ 4-Methyl-*a*-naphthylmethyl bromide (SHOESMITH and RUBLI), 3102.
$C_{12}H_{12}O_2$ Methoxy-*a*-naphthylcarbinols (SHOESMITH and RUBLI), 3102.
$C_{12}H_{12}N_2$ Harmalan (MANSKE, PERKIN, and ROBINSON), 11.
$C_{12}H_{14}O_5$ Ethyl 2-hydroxy-1:5-*iso*phthalate (CHATTAWAY and PRATS), 690.
Methyl 6-methoxymethylhomopiperonylate (STEVENS), 185.
$C_{12}H_{14}O_6$ 4:5-Dimethoxy-2:6-diacetylresorcinol (CHAPMAN, PERKIN, and ROBINSON), 3033.
$C_{12}H_{15}N$ *trans*-Hexahydrocarbazole, and its picrate (GURNEY, PERKIN, and PLANT), 2676.
$C_{12}H_{15}N_3$ 5-Keto-6-methyl-2:3:4:5-tetrahydropyridine 5-phenylhydrazone, and its hydrochloride (MANSKE, PERKIN, and ROBINSON), 9.
$C_{12}H_{16}O_4$ Ethyl β-*m*-methoxyphenoxypropionate (PERKIN, RÂY, and ROBINSON), 2097.
Ethyl phenylmalonate, nitration of (BAKER and INGOLD), 835.
$C_{12}H_{16}O_5$ 4-Acetoxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylic acid (BHAGVAT and SIMONSEN), 83.
$C_{12}H_{18}N_2$ Aminohexahydrocarbazoles (GURNEY and PLANT), 1317.
$C_{12}H_{17}N$ 4-Phenyl-1-methylpiperidine, and its salts (MILLS, PARKIN, and WARD), 2618.
$C_{12}H_{18}O_2$ β-Thujylideneacetic acid (HUGH and KON), 2597.
Acid, and its silver salt, from dehydration of ethyl thujolacetate (HUGH and KON), 2598.

$C_{12}H_{18}O_3$ 4-Methyl-5-*cyclo*hexane*spirocyclo*pentan-3-one-1-carboxylic acid (INGOLD and SEELEY), 1689.

$C_{12}H_{18}O_4$ *l*-4-Acetyl-2:2:3-trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid (BHAGVAT, SIMONSEN, and RAO), 88.

$C_{12}H_{18}O_6$ 1-Acetoxy-4:4:5-trimethyl*cyclo*pentane-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 84.

γ-Mannonolactone-diacetone (GOODYEAR and HAWORTH), 3143.

$C_{12}H_{19}N$ β-Phenylethyldimethylethylamine, picrate of (HANHART and INGOLD), 1008.

$C_{12}H_{20}O_4$ Ethyl 2:3-dimethyl*cyclo*butane-1:4-dicarboxylate (VOGEL), 1992.

$C_{12}H_{20}N$ γ-Phenylpropyltrimethylamine, picrate of (INGOLD and WILSON), 810.

$C_{12}H_{20}Br_2$ $\epsilon\zeta$-Dibromo-$\delta\eta$-dimethyl-$\Delta\gamma\eta$-decadiene (FARMER, LAROIA, SWITZ, and THORPE), 2957.

$C_{12}H_{22}O_2$ 5-Acetyl-1:3:3:4:4-pentamethyl*cyclo*pentan-1-ol (VOGEL), 598.

$\delta\eta$-Dimethyl-$\Delta\gamma\eta$-decadiene-$\epsilon\zeta$-diol (FARMER, LAROIA, SWITZ, and THORPE), 2957.

$C_{12}H_{22}O_4$ Ethyl $\beta\beta'$-dimethyladipate (VOGEL), 1991.

Ethyl hydrogen *iso*heptylmalonate (KON and MAR), 1554.

$C_{12}H_{22}O_{11}$ Cellobiose, constitution of (HAWORTH, LONG, and PLANT), 2809.

Lactose, constitution of (HAWORTH and LONG), 544.

Maltose, constitution of (HAWORTH, LOACH, and LONG), 3146.

Melibiose, constitution of (CHARLTON, HAWORTH, and HICKINBOTTOM), 1527; (HAWORTH, LOACH, and LONG), 3146.

Sucrose, constitution of (HAWORTH, HIRST, and NICHOLSON), 1513; (AVERY, HAWORTH, and HIRST), 2308; vapour pressures of mixtures of methyl acetate, water, and (MCKEOWN and STOWELL), 97.

Turanose (LEITCH), 588.

$C_{12}H_{24}N_2$ Pinacolinazine (BAIRD and WILSON), 2116.

12 III

$C_{12}H_6O_8N_4$ Tetranitrodiphenyl (BLAKEY and SCARBOROUGH), 3006.

$C_{12}H_6Cl_4S_2$ 2:5-Dichlorophenyl trisulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_6Br_4S_2$ 2:5-Dibromophenyl trisulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_7OBr_3$ 3:5:4'-Tribromo-4-hydroxydiphenyl (BELL and ROBINSON), 1131.

$C_{12}H_7O_2N$ 1-Cyano-8-naphthoic acid (DAVIES and LEEPER), 1126.

$C_{12}H_7NBr_4$ Tetrabromo-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3005.

$C_{12}H_8OBr_2$ 3:4'-Dibromo-4-hydroxydiphenyl (BELL and ROBINSON), 1131.

$C_{12}H_8O_6N_4$ 2':3:4'-Trinitro-4-aminodiphenyl (LE FÈVRE, MOIR, and TURNER), 2337.

$C_{12}H_8NCl_3$ 2':4:4'-Trichloro-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3004.

$C_{12}H_8NBr_3$ 2:4:6-Tribromo-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3008.

$C_{12}H_9OBr$ Bromo-4-hydroxydiphenyls (BELL and ROBINSON), 1131.

$C_{12}H_9O_2Cl$ 3-Methoxy-α-naphthoyl chloride (SHOESMITH and RUBLI), 3101.

$C_{12}H_9O_4N_3$ Dinitro-2-aminodiphenyl (SCARBOROUGH and WATERS), 96.

$C_{12}H_9O_6N_5$ 2:3:5'-Trinitrobenzidine (LE FÈVRE, MOIR, and TURNER), 2333.

$C_{12}H_9NCl_2$ 3:5-Dichloro-2-aminodiphenyl, and its hydrochloride (SCARBOROUGH and WATERS), 92.

$C_{12}H_9NBr_2$ 3:5-Dibromo-2-aminodiphenyl (SCARBOROUGH and WATERS), 95.

$C_{12}H_{10}O_2N_2$ 4'-Nitro-2-aminodiphenyl (SCARBOROUGH and WATERS), 96.

Nitro-3-aminodiphenyls (BLAKEY and SCARBOROUGH), 3008.

γ-Phthalimidobutyronitrile, preparation of (MANSKE, PERKIN, and ROBINSON), 6.

$C_{12}H_{10}NCl$ Chloro-3-aminodiphenyls (BLAKEY and SCARBOROUGH), 3003.

$C_{12}H_{10}NBr$ 5-Bromo-2-aminodiphenyl, and its hydrochloride (Scarborough and Waters), 94.

Bromo-3-aminodiphenyls (Blakey and Scarborough), 3005.

$C_{12}H_{10}Cl_2Si$ Diphenylsilicon dichloride, preparation of (Kipping and Murray), 2734.

$C_{12}H_{11}OBr$ Methoxy-*α*-naphthylmethyl bromides (Shoesmith and Rubli), 3101.

$C_{12}H_{11}O_2N$ Methoxy-1-naphthaldoximes (Brady and Goldstein), 1962.

$C_{12}H_{11}O_4N$ Methyl 3-hydroxyindole-2-carboxylate (Robertson), 1939.

$C_{12}H_{11}O_4N_3$ 1-Phenyl-4-acetylamino-5-ketopyrazoline-3-carboxylic acid (Chattaway and Humphrey), 2136.

$C_{12}H_{11}O_6N$ Methyl nitrobenzylidenemalonates (Baker and Eccles), 2126.

$C_{12}H_{13}O_2N$ Methyl *β*-3-indolylpropionate (Manske and Robinson), 241.

$C_{12}H_{13}O_2N_3$ 1-Nitroanilino-1-cyano*cyclo*pentanes (Oakeshott and Plant), 491.

$C_{12}H_{13}O_3N$ 1-Acetyl-5:6-dimethoxyindole (Oxford and Raper), 421.

$C_{12}H_{13}O_6N$ Methyl nitrobenzylmalonates (Baker and Eccles), 2127.

$C_{12}H_{14}O_2N_2$ Nitrohexahydrocarbazoles (Gurney and Plant), 1317.

$C_{12}H_{14}O_4N_2$ 1-Nitroanilino*cyclo*pentane-1-carboxylic acids (Oakeshott and Plant), 492.

$C_{12}H_{14}NBr$ 6-Bromohexahydrocarbazole, and its hydrobromide (Gurney and Plant), 1321.

$C_{12}H_{14}N_3Cl$ 5-Keto-6-methyl-2:3:4:5-tetrahydropyridine 5-*m*-chlorophenylhydrazone, and its hydrochloride (Manske, Perkin, and Robinson), 10.

$C_{12}H_{15}O_3N_3$ 1-Nitroanilino*cyclo*pentane-1-carboxyamides (Oakeshott and Plant), 491.

$C_{12}H_{16}O_4N_2$ 8-Nitro-5:6-dimethoxy-2-methyl-1:2:3:4-tetrahydro*iso*quinoline (Haworth), 2284.

$C_{12}H_{17}O_2N$ 5:6-Dimethoxy-2-methyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (Haworth), 2283.

$C_{12}H_{17}O_3N_3$ Propylvanillin semicarbazones (Dickinson, Heilbron, and Irving), 1895.

$C_{12}H_{17}O_4N$ Methyl ethyl *β*-cyano-Δ^{δ}-hexene-$\beta\zeta$-dicarboxylate (Farmer and Healey), 1065.

$C_{12}H_{17}N_3S$ Acetone *δ*-*α*-phenylethylthiosemicarbazone (Baird, Burns, and Wilson), 2532.

Benzaldehyde *S*-butylthiosemicarbazone (Baird, Burns, and Wilson), 2530.

$C_{12}H_{19}O_2N_3$ Nitrophenylpropyltrimethylamines, picrates of (Ingold and Wilson), 811.

$C_{13}H_{20}NI$ *β*-Phenylethyldimethylethylammonium iodide (Hanhart and Ingold), 1007.

$C_{12}H_{24}O_2N_2$ *n*-Decanedicarboxyamide (Barnicoat), 2928.

12 IV

$C_{12}H_3ONCl_6$ Hexachlorobenzoquinoneanil (Bradfield, Cooper, and Orton), 2858.

$C_{12}H_4ONCl_5$ 2:6:2′:4′:6′-Pentachlorobenzoquinoneanil (Bradfield, Cooper, and Orton), 2858.

$C_{12}H_4ONCl_7$ Heptachloro-4-hydroxydiphenylamine (Bradfield, Cooper, and Orton), 2859.

$C_{12}H_4ONBr_5$ Pentabromobenzoquinoneanil (Bradfield, Cooper, and Orton), 2861.

$C_{12}H_5ONCl_4$ 2:6:2′:4′-Tetrachlorobenzoquinoneanil (Bradfield, Cooper, and Orton), 2857.

$C_{12}H_5ONCl_6$ Hexachlorohydroxydiphenylamine (Bradfield, Cooper, and Orton), 2858.

$C_{12}H_5O_2NCl_4$ Tetrachloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{12}H_6ONCl_3$ 2:2′:4′-Trichlorobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2857.
$C_{12}H_5ONCl_5$ 2:6:2′:4′:6′-Pentachloro-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.
$C_{12}H_5ONBr_5$ Pentabromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2861.
$C_{12}H_6O_2NCl_3$ Trichloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{12}H_6O_5N_2Cl_2$ Dinitro-4:4′-dichlorodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1172.
$C_{12}H_6O_5N_2Br_2$ Dibromodinitrodiphenyl ethers (LE FÈVRE, SAUNDERS, and TURNER), 1171.
$C_{12}H_6O_5N_2Te$ Dinitrophenoxtellurines (DREW and THOMASON), 122.
$C_{12}H_7ONCl_2$ 2′:4′-Dichloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{12}H_7O_3NBr_2$ 3:4′-Dibromo-5-nitro-4-hydroxydiphenyl (BELL and ROBINSON), 1131.
Nitro-4:4′-dibromodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1172.
$C_{12}H_7O_3NTe$ Nitrophenoxtellurines (DREW and THOMASON), 121.
$C_{12}H_7O_4N_2Br$ 4-Bromo-3:4′-dinitrodiphenyl (LE FÈVRE, MOIR, and TURNER), 2336.
$C_{12}H_7O_5N_2Br$ 5-Bromo-3:4′-dinitro-4-hydroxydiphenyl (BELL and ROBINSON), 1133.
$C_{12}H_8ONCl$ 4′-Chlorobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2856.
$C_{12}H_8ONCl_3$ 2:2′:4′-Trichloro-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.
$O_{12}H_8ONBr$ 4′-Bromobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2860.
$C_{12}H_8O_2NCl$ 4′-Chloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3003.
$C_{12}H_8O_2NBr$ 4′-Bromo-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
Bromonitrodiphenyls (SCARBOROUGH and WATERS), 96, 1138.
$C_{12}H_8O_2N_2Br_2$ 5:4′-Dibromo-3-nitro-4-aminodiphenyl (SCARBOROUGH and WATERS), 1138.
$C_{12}H_8O_3NBr$ 4-Bromo-4′-nitrodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1171.
Bromonitro-4-hydroxydiphenyls (BELL and ROBINSON), 1132.
$C_{12}H_9ONTe$ 2-Aminophenoxtellurine (DREW and THOMASON), 124.
$C_{12}H_9O_2N_2Cl$ 4′-Chloro-3-nitro-4-aminodiphenyl (SCARBOROUGH and WATERS), 1138.
$C_{12}H_9O_2N_2Br$ 4-Bromo-4′-nitro-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3009.
Bromonitro-4-aminodiphenyls (SCARBOROUGH and WATERS), 1138.
$C_{12}H_9O_4N_2As$ Nitrophenarsazinic acid (GIBSON and JOHNSON), 2514.
$C_{12}H_{10}ONCl$ 4-Chloro-4′-aminodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1172.
4′-Chloro-4-hydroxydiphenylamine, and its toluenesulphonate (BRADFIELD, COOPER, and ORTON), 2856.
$C_{12}H_{10}ONBr$ 4′-Bromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.
$C_{12}H_{10}ON_2Te$ Diaminophenoxtellurines (DREW and THOMASON), 124.
$C_{12}H_{10}O_5Cl_6S$ Ethyl anhydro-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphonate (CHATTAWAY and MORRIS), 2017.
$C_{12}H_{11}O_3N_3S$ Ethyl penthian-4-one-3-carboxylate p-nitrophenylpyrazolone (BENNETT and SCORAH), 198.
$C_{12}H_{11}O_3N_2As$ Nitrodiphenylamine-6′-arsinic acids (GIBSON and JOHNSON), 2513.

$C_{12}H_{11}O_6N_2Cl$ Nitrobenzylpyridinium perchlorates (POLLARD and ROBINSON), 2778.

$C_{12}H_{12}ON_2S$ Ethyl penthian-4-one-3-carboxylate phenylpyrazolone (BENNETT and SCORAH), 198.

$C_{12}H_{12}O_3NAs$ Diphenylamine-*o*-arsinic acid (GIBSON and JOHNSON), 2507.

$C_{12}H_{13}O_2NS$ Acetyl-4-keto-2-methyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2749.

$C_{12}H_{14}O_2NCl$ 1-Chloroanilino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 490.

$C_{12}H_{14}O_2NBr$ 1-Bromoanilino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 490.

$C_{12}H_{14}O_2N_2Cl_2$ *n*-Butyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.

$C_{12}H_{15}ON_2Cl$ 1-Chloroanilino*cyclo*pentane-1-carboxyamides (OAKESHOTT and PLANT), 490.

$C_{12}H_{16}O_2NI$ 5:6-Dimethoxy-3:4-dihydro*iso*quinoline methiodide (HAWORTH), 2283.

$C_{12}H_{20}ONI$ *l*-Methylephedrine methiodide (SMITH), 2057.

12 V

$C_{12}H_4ONCl_2Br_3$ Dichlorotribromobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2862.

$C_{12}H_4ONCl_3Br_2$ Trichlorodibromobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2863.

$C_{12}H_4ONCl_3Br_4$ Trichlorotetrabromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2864.

$C_{12}H_6ONCl_2Br_3$ Dichlorotribromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{12}H_6ONCl_3Br_2$ Trichlorodibromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{12}H_7ONCl_3Br$ Trichlorobromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2863.

$C_{12}H_7O_2NCl_2S_2$ 2:5-Dichlorophenyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_7O_2NBr_2S_2$ 2:5-Dibromophenyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_8O_2N_2ClAs$ Chloronitrodihydrophenarsazines (GIBSON and JOHNSON), 2514.

$C_{12}H_8O_2N_2BrAs$ Bromonitro-5:10-dihydrophenarsazine (GIBSON and JOHNSON), 2514.

$C_{12}H_8O_4NClS_2$ 4-Chlorobenzenesulphonyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{12}H_8O_2N_2Cl_2As$ 2-Nitrodiphenylamine-6′-dichloroarsine (GIBSON and JOHNSON), 2513.

$C_{12}H_{11}ON_2BrS$ Ethyl penthian-4-one-3-carboxylate *p*-bromophenylpyrazolone (BENNETT and SCORAH), 198.

$C_{12}H_{17}O_2NBrI$ Trimethyl-6-bromo-β-piperonylethylammonium iodide (STEVENS), 184.

C_{13} Group.

$C_{13}H_{14}O_4$ 4-Methyl-5-*cyclo*hexane*spiro*-(0:1:2)-*dicyclo*pentan-3-one-1:2-dicarboxylic anhydride (INGOLD and SEELEY), 1688.

$C_{13}H_{18}O_3$ 3-Methoxy-4-ethoxystyryl methyl ketone (DICKINSON, HEILBRON, and IRVING), 1894.

$C_{13}H_{16}O_5$ 4-Methyl-5-*cyclo*hexane*spiro*-(0:1:2)-*dicyclo*pentan-3-one-1:2-dicarboxylic acid (INGOLD and SEELEY), 1688.

$C_{13}H_{18}O_3$ Ethyl benzyloxybutyrate (BENNETT and HOCK), 475.

$C_{13}H_{19}N$ 1-β-Phenylethylpiperidine, and its picrate (POLLARD and ROBINSON), 2779.

4-Phenyl-1-ethylpiperidine, and its hydrochloride (MILLS, PARKIN, and WARD), 2618.

$C_{13}H_{20}O$ 2-*iso*Propylidene-β-thujone (HUGH and KON), 2599.

$C_{13}H_{20}O_2$ *cyclo*Hexane*spiro*-2-ethyl*cyclo*hexane-3:5-dione (KON and NARAYANAN), 1542.

$C_{13}H_{20}O_5$ Ethyl 3:3-dimethyl*cyclo*pentan-2-one-1:4-dicarboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3012.

$C_{13}H_{22}O_2$ Ethyl dehydroundecenoate, and its metallic derivatives (MYDDLETON and BERCHEM), 1928.

13 III

$C_{13}H_8OS_2$ 1:3-Benzdithiole-2-*p*-benzoquinone, and its hydrochloride (HURTLEY and SMILES), 536.

$C_{13}H_8O_2Cl_2$ 3:5-Dichloro-4-hydroxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2868.

$C_{13}H_8O_2I_2$ 3:5-Di-iodo-4-hydroxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{13}H_8O_6N_2$ Dinitro-4-hydroxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2871.

$C_{13}H_9O_2I$ 3-Iodo-4-hydroxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{13}H_9NSe$ Phenylbenzselenazole, and its chloroplatinate (CLARK), 2807.

$C_{13}H_{10}OS_2$ 2-*p*-Hydroxyphenyl-1:3-benzdithiole, and its nitrate (HURTLEY and SMILES), 536.

$C_{13}H_{10}O_4Cl_6$ Ethyl ester of anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{13}H_{10}O_5N_4$ 3-Nitro-4-hydroxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2380.

$C_{13}H_{10}O_6Cl_2$ ωω-Dichloro-5-carboxy-2-acetoxyacetophenone (CHATTAWAY and PRATS), 691.

$C_{13}H_{11}OAs$ 10-Methylphenoxarsine (AESCHLIMANN), 414.

$C_{13}H_{11}O_3N_3$ 3-Nitro-4-nitrosomethylaminodiphenyl (BELL and ROBINSON), 1130.

$C_{13}H_{11}O_4N_3$ 2:5-Dihydroxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2340.

$C_{13}H_{11}O_4N_5$ 3-Nitro-4-aminobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 23.

$C_{13}H_{11}O_7N_5$ 3:5-Diketo-2-*p*-nitrophenyltetrahydro-1:2:4-triazine-6-carboxylic acid urethane (WHITELEY and YAPP), 527.

$C_{13}H_{12}ON_2$ Harmine (MANSKE, PERKIN, and ROBINSON), 1.

$C_{13}H_{12}O_2N_2$ 3-Benzeneazo-2:6-dimethylpyrone (MULLEN and CROWE), 1753.

$C_{13}H_{12}O_4N_2$ 5-Methoxysalicylaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2340.

$C_{13}H_{12}O_5N_4$ 3:5-Diketo-2-phenyltetrahydro-1:2:4-triazine-6-carboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{13}H_{12}N_2S$ 2-Dimethylamino-β-naphthathiazole (HUNTER and STYLES), 1213.

$C_{13}H_{13}NAs$ 10-Methyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.

$C_{13}H_{13}O_2N$ Methylmethoxy-1-naphthaldoximes (BRADY and GOLDSTEIN), 1963.

$C_{13}H_{13}O_2As$ 10-Methylphenoxarsine dihydroxide (AESCHLIMANN), 414.

$C_{13}H_{13}O_6N_3$ Ethyl 2:4-dinitrophenylethylcyanoacetate, and its silver salt (FAIRBOURNE and FAWSON), 48.

$C_{13}H_{14}ON_2$ Harmaline (MANSKE, PERKIN, and ROBINSON), 1.

$C_{13}H_{14}O_2N_2$ Nitro-β-naphthyltrimethylamine, salts of (INGHAM), 1974.

$C_{13}H_{14}O_3N_2$ 10-Nitro-ψ-indoxyl*spirocyclo*hexane (BETTS, MUSPRATT, and PLANT), 1313.

$C_{13}H_{14}O_5N_2$ Ethyl hydrogen diketosuccinate tolylhydrazones (CHATTAWAY and HUMPHREY), 2794.

$C_{13}H_{14}O_7N_2$ 3-Nitro-4-acetamidobenzylidene diacetate (HODGSON and BEARD), 22.

$C_{13}H_{14}NI$ Lepidine alliodide (HAMER), 2802.

$C_{13}H_{14}N_2S$ *s*-α-Naphthyldimethylthiocarbamide (HUNTER and STYLES), 1213.

$C_{13}H_{15}ON$ ψ-Indoxyl*spirocyclo*hexane, and its sodium salt (BETTS, MUSPRATT, and PLANT), 1313.

*cyclo*Pentenylacetanilide (KON and NARAYANAN), 1547.

*cyclo*Pentylideneacetanilide (KON and NARAYANAN), 1547.

$C_{13}H_{15}O_4N$ 1-Carboxyanilino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 493.

$C_{13}H_{15}O_5N$ Ethyl *p*-nitrobenzylacetoacetate (BURGESS), 2019.

$C_{13}H_{15}O_5Br$ 2-Bromo-4-methyl-5-*cyclo*hexane*spiro*-(0:1:2)*dicyclo*pentan-3-one-1:2-dicarboxylic acid (INGOLD and SEELEY), 1689.

$C_{13}H_{16}O_2N_2$ 5-Nitro-9-methylhexahydrocarbazole (GURNEY and PLANT), 1318.

$C_{13}H_{16}O_3N_2$ 1-Carboxyanilino*cyclo*pentane-1-carboxyamides (OAKESHOTT and PLANT), 492.

$C_{13}H_{17}O_2N$ 1-Anilino*cyclo*hexane-1-carboxylic acid (BETTS, MUSPRATT, and PLANT), 1312.

1-Toluidino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 486.

Substance, from salicylaldehyde and β-hydroxylamino-βγ-dimethyl-Δγ-butene (EARL and KENNER), 2142.

$C_{13}H_{17}O_3N$ 1-*p*-Anisidino*cyclo*pentane-1-carboxylic acid (OAKESHOTT and PLANT), 488.

$C_{13}H_{17}O_3N_3$ 3:4-Dimethoxystyryl methyl ketone semicarbazone (DICKINSON, HEILBRON, and IRVING), 1892.

$C_{13}H_{18}ON_2$ 1-Anilino*cyclo*hexane-1-carboxylamide (BETTS, MUSPRATT, and PLANT), 1311.

$C_{13}H_{19}O_4N$ Methyl ethyl β-cyano-γ-methyl-Δ$^{\delta}$-hexene-βζ-dicarboxylate (FARMER and HEALEY), 1065.

$C_{13}H_{20}NI$ Benzylmethylpiperidinium iodide (POLLARD and ROBINSON), 2776.

$C_{13}H_{21}O_3N_3$ 4-Methyl-5-*cyclo*hexane*spirocyclo*pentan-3-one-1-carboxylic acid semicarbazone (INGOLD and SEELEY), 1689.

$C_{13}H_{23}O_4N_5$ Methyl 4-hydroxy-2:2:3-trimethyl-Δ^{3}-*cyclo*hexen-5-one-1-carboxylate disemicarbazone (BHAGVAT and SIMONSEN), 83.

$C_{13}H_{25}O_3N_3$ 5-Acetyl-1:3:3:4:4-pentamethyl*cyclo*pentan-1-ol semicarbazones (VOGEL), 598.

13 IV

$C_{13}H_6ON_3Cl_2$ *cycloazi*-2:4:6-Trichlorophenylbenztriazone (CHATTAWAY and WALKER), 329.

$C_{13}H_7ON_3Cl_2$ *cycloazi*-2:4-Dichlorophenylbenztriazone (CHATTAWAY and WALKER), 328.

$C_{13}H_7ON_3Br_2$ 2:4-Dibromophenylbenztriazones (CHATTAWAY and WALKER), 329.

$C_{13}H_8ONCl_3$ 2:4:6-Trichlorobenzanilide (CHAPMAN), 1749.

$C_{13}H_8ON_3Br$ *p*-Bromophenylbenztriazones (CHATTAWAY and WALKER), 328.

$C_{13}H_8O_4N_2Cl_2$ 4:4′-Dichloro-3:3′-dinitrodiphenylmethane (LE FÈVRE and TURNER), 1120.

$C_{13}H_8O_7N_5Br$ 2:4:6-Trinitro-3-hydroxybenzaldehyde *p*-bromophenylhydrazone (HODGSON and BEARD), 2379.

$C_{13}H_8O_8N_4S$ *s*-Bis-3:5-dinitrophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.

$C_{13}H_8N_2Br_4S$ *s*-Di-2:5-dibromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.

$C_{13}H_9ONCl_2$ *o*-Hydroxybenzylidenedichloroanilines (ROBERTS and TURNER), 1843.

$C_{13}H_9O_3N_2Cl_2$ 3:4-Dichlorobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 25.

2:4-Dichlorodiazoaminobenzene-2′-carboxylic acid (CHATTAWAY and WALKER), 333.

$C_{13}H_9O_2N_2Br_2$ 3:4-Dibromobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 26.

2:4-Dibromodiazoaminobenzene-2′-carboxylic acid (CHATTAWAY and WALKER), 332.

$C_{13}H_9O_2N_2I_2$ 3:4-Di-iodobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 27.

$C_{13}H_9O_3N_2Br_2$ *β-o*-Nitrobenzoyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 331.

$C_{13}H_9O_5N_4Br$ Dinitrohydroxybenzaldehyde *p*-bromophenylhydrazones (HODGSON and BEARD), 2379.

$C_{13}H_9O_4N_4Cl$ 4-Chloro-3-nitrobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 24.

$C_{13}H_9O_4N_4Br$ 4-Bromo-3-nitrobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 24.

$C_{13}H_9O_4N_4I$ 4-Iodo-3-nitrobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 25.

$C_{13}H_{10}ONCl$ *o*-Hydroxybenzylidene-3-chloroaniline (ROBERTS and TURNER), 1843.

$C_{13}H_{10}ONAs$ 9-Methylcarbazole-3-arsenious oxide (BURTON and GIBSON), 2387.

$C_{13}H_{10}O_3Cl_2S_2$ 4-Toluenesulphonyl-2:5-dichlorophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{13}H_{10}O_3N_2Cl$ Chlorohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 1741.

$C_{13}H_{10}O_3N_2Br$ Bromohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 3041.

3-Nitro-4-hydroxybenzaldehyde *p*-bromophenylhydrazone (HODGSON and BEARD), 2380.

$C_{13}H_{10}O_3N_2I$ Iodohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 3043.

$C_{13}H_{10}O_4N_2S$ *m*-Nitrophenylnitrobenzylsulphones (CHATTERJEE and ROBINSON), 2782.

$C_{13}H_{10}NCl_2As$ 9-Methylcarbazole-3-arsenious chloride (BURTON and GIBSON), 2387.

$C_{13}H_{10}N_2Br_2S$ *s*-Di-*o*-bromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.

$C_{13}H_{11}ON_2Br_2$ *o*-Aminobenzoyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 330.

$C_{13}H_{11}O_4NS$ *m*-Nitrophenylbenzylsulphone (CHATTERJEE and ROBINSON), 2782.

$C_{13}H_{11}O_4NS_2$ 4-Toluenesulphonyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{13}H_{11}NClAs$ 10-Chloro-4-methyl-5:10-dihydrophenarsazine (GIBSON and JOHNSON), 2510.

$C_{13}H_{11}NBrAs$ 10-Bromomethyl-5:10-dihydrophenarsazines (GIBSON and JOHNSON), 2509.

$C_{13}H_{12}ONBr$ Aceto-4-bromo-2-methyl-α-naphthalide (SHOESMITH and RUBLI), 3103.

$C_{13}H_{12}O_2NAs$ Methylphenarsazinic acids, and their salts (GIBSON and JOHNSON), 2509.

$C_{13}H_{12}O_3NAs$ 9-Methylcarbazole-3-arsinic acid (BURTON and GIBSON), 2386.
$C_{13}H_{12}O_4N_2S$ *p*-Toluenesulphon-2-nitroanilide (BELL and ROBINSON), 1129.
$C_{13}H_{12}O_5NAs$ Carboxydiphenylamine-6′-arsinic acids (BURTON and GIBSON), 248.
$C_{13}H_{12}O_{13}N_4As_2$ *s*-Carbamido-5-nitro-4-amino-2-hydroxyphenylarsinic acid, and its salts (KING), 1056.
$C_{13}H_{13}N_2Br_4S$ 2-Dimethylamino-β-naphthathiazole tetrabromide (HUNTER and STYLES), 1213.
$C_{13}H_{14}O_3NAs$ Methyldiphenylaminearsinic acids (GIBSON and JOHNSON), 2508.
$C_{13}H_{14}O_9N_2As_2$ *s*-Carbamido-4-amino-2-hydroxyphenylarsinic acid (KING), 1055.
$C_{13}H_{15}ONS$ 3-Keto-2-benzyl-2:3-dihydro-1:4-benzthiazine (MILLS and WHITWORTH), 2748.
$C_{13}H_{15}O_3NS$ Ethyl 3-keto-2:3-dihydro-1:4-benzthiazine-2-propionate (MILLS and WHITWORTH), 2745.
Ethyl 4-ketotetrahydro-1:5-heptabenzthiazine-2-acetates (MILLS and WHITWORTH), 2743.
$C_{13}H_{16}O_9N_4As_2$ *s*-4-Carbamido-4:5-diamino-2-hydroxyphenylarsinic acid (KING), 1056.
$C_{13}H_{18}O_3N_2S$ Nitrophenyl β-piperidinoethyl sulphides (BENNETT and BERRY), 1680.
$C_{13}H_{18}O_5N_2S$ 1-*o*-Anisidino*cyclo*pentane-1-carboxyamide-5′-sulphonic acid, sodium salt (OAKESHOTT and PLANT), 488.
$C_{13}H_{19}O_2N_2I$ Nitrobenzylmethylpiperidinium iodides (POLLARD and ROBINSON), 2777.
$C_{13}H_{19}O_4N_2As$ 3-Acetamido-4-piperidinophenylarsinic acid (KING), 1053.

13 V

$C_{13}H_9O_2NClAs$ 10-Chloro-5:10-dihydrophenarsazinecarboxylic acids (BURTON and GIBSON), 249.
$C_{13}H_9O_2N_3ClBr$ Chlorobromobenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 25.
$C_{13}H_9O_2N_3ClI$ Chloroiodobenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 26.
$C_{13}H_9O_2N_3BrI$ Bromoiodobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 26.
$C_{13}H_{10}O_4NClS_2$ 4-Toluenesulphonyl 4-chloro-2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

13 VII

$C_{13}H_{26}O_4N_3Cl_4BrSPt$ Tetrachloro(triaminopropane-α-bromocamphor-π-sulphonate) platinum (MANN), 1231.

C_{14} Group.

$C_{14}H_{10}$ Phenanthrene, synthesis of (KENNER and WILSON), 1103.

14 II

$C_{14}H_8O_4$ Quinizarin, structure of (GREEN), 2384.
$C_{14}H_{10}O_2$ Benzil, surface tension and density of (GARNER and SUGDEN), 2882.
Dihydroxyanthracenes (GREEN), 555.
$C_{14}H_{10}O_5$ *o*-Benzoylphloroglucinaldehyde (ROBERTSON and ROBINSON), 1713.
Di-*p*-carboxydiphenyl ether, and its silver salt (REILLY, DRUMM, and BARRETT), 70.
1:3-Dihydroxy-7-methoxyxanthone (SHINODA), 1985.
$C_{14}H_{12}O_3$ 1-Methoxydiphenyl-1′-carboxylic acid (RULE and BRETSCHER), 926.
4-Methoxyphenyl benzoate (IRVINE and SMITH), 75.
$C_{14}H_{12}Br_2$ 2:2′-Dibromodibenzyl (KENNER and WILSON), 1111.
$C_{14}H_{14}O$ Di-*p*-tolyl ether (REILLY, DRUMM, and BARRETT), 67.
$C_{14}H_{14}O_2$ *iso*Hydrobenzoins (READ and STEELE), 917.

$C_{14}H_{14}Se$ Di-*o*-tolyl selenide (PORRITT), 29.

$C_{14}H_{16}Si$ Diphenyldimethylsilicane (KIPPING), 107.

$C_{14}H_{18}O_3$ 3-Methoxy-4-propoxystyryl methyl ketones (DICKINSON, HEILBRON, and IRVING), 1895.

$C_{14}H_{18}O_{10}$ Tetra-acetyl γ-mannolactone (GOODYEAR and HAWORTH), 3144.

$C_{14}H_{21}N$ 1-γ-Phenylpropylpiperidine, and its picrate (POLLARD and ROBINSON), 2780.

4-Phenyl-1-*n*-propylpiperidine, and its hydrochloride (MILLS, PARKIN, and WARD), 2619.

$C_{14}H_{24}O_4$ *dl-iso*Menthyl hydrogen succinate (READ, ROBERTSON, and COOK), 1238.

14 III

$C_{14}H_5O_9N_3$ Trinitrofluorenone-4-carboxylic acid (BELL and ROBINSON), 2238.

$C_{14}H_6O_7N_2$ 4:4′-Dinitrodiphenic anhydride (BELL and ROBINSON), 1697.

$C_{14}H_6O_{10}N_4$ 3:5:3′:5′-Tetranitrobenzil (CHATTAWAY and COULSON), 578.

$C_{14}H_7O_5N$ Nitrodiphenic anhydrides (BELL and ROBINSON), 1697, 2236.
Nitrofluorenone-4-carboxylic acid (BELL and ROBINSON), 2238.

$C_{14}H_8ON_4$ *p*-Azoxybenzonitrile (NISBET), 2084.

$C_{14}H_8O_3S$ Thionyldihydroxyanthracenes (GREEN), 557, 2344.

$C_{14}H_9O_2Cl$ 4-Chloro-1:9-dihydroxyanthracene (GREEN), 2343.

$C_{14}H_9O_3Cl$ Chlorohydroxybenzaldehyde benzoates (HODGSON and JENKINSON), 1741.

$C_{14}H_9O_3Br$ 4-Bromo-2-hydroxybenzaldehyde benzoate (HODGSON and JENKINSON), 3041.

$C_{14}H_9O_3I$ Iodohydroxybenzaldehyde benzoates (HODGSON and JENKINSON), 3043.

$C_{14}H_9O_6N_3$ Dinitrobenzylidenephenylnitromethane (BAKER and WILSON), 847.
2:4:4′-Trinitrostilbene (NISBET), 2082.

$C_{14}H_9O_8N_3$ Trinitro-4-methoxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2872.

$C_{14}H_{10}O_2Cl_2$ 3:5-Dichloro-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2867.

$C_{14}H_{10}O_4N_2$ *p*-Nitrobenzylidenephenylnitromethane (BAKER and WILSON), 844.

$C_{14}H_{10}O_6N_2$ Dinitro-4-methoxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2871.

$C_{14}H_{10}O_6Cu$ Cuprisalicylic acid, sodium salt (WARK), 1756.

$C_{14}H_{10}O_9N_4$ Tetranitrodi-*p*-tolyl ether (REILLY, DRUMM, and BARRETT), 73.

$C_{14}H_{10}NCl_3$ 2′:4:4′-Trichloro-3-acetamidodiphenyl (BLAKEY and SCARBOROUGH), 3004.

$C_{14}H_{11}O_2Cl$ 3-Chloro-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2867.

$C_{14}H_{11}O_2Br$ 3-Bromo-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2868.

$C_{14}H_{11}O_2I$ 3-Iodo-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2869.

$C_{14}H_{11}O_3Br$ Bromomethoxyphenyl benzoates (IRVINE and SMITH), 75.

$C_{14}H_{11}O_4N$ Nitro-4-methoxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{14}H_{11}O_5N_3$ Dinitro-3-acetamidodiphenyl (SCARBOROUGH and WATERS), 96.
Nitrobenzylnitrobenzaldoximes (BRADY and KLEIN), 879.

$C_{14}H_{11}O_7N_5$ 4:6-Dinitro-3-methoxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2381.

$C_{14}H_{12}OS_2$ 2-*p*-Methoxyphenyl-1:3-benzdithiole, and its nitrate (HURTLEY and SMILES), 536.

$C_{14}H_{12}O_3N_2$ 5-Carboxy-2-ethoxyphenylglycollic acid phenylhydrazone (CHATTAWAY and PRATS), 690.

4'-Nitro-2-acetamidodiphenyl (SCARBOROUGH and WATERS), 96.

Nitro-3-acetamidodiphenyls (BLAKEY and SCARBOROUGH), 3008.

β-O-p-Nitrobenzylbenzaldoxime (BRADY and KLEIN), 885.

$C_{14}H_{12}O_4N_2$ 3-Nitro-4-methoxybenzanilide (BLAKEY, JONES, and SCARBOROUGH), 2870.

3-Nitro-4-methoxybenzophenoneoxime (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{14}H_{12}O_5N_2$ Dinitrodi-*p*-tolyl ethers (REILLY, DRUMM, and BARRETT), 72.

$C_{14}H_{13}ON$ *N*-Methylbenziminophenyl ether (CHAPMAN), 1747.

$C_{14}H_{13}O_2Cl$ Chloro-2-benzyloxyanisoles (OXFORD and ROBINSON), 2241.

$C_{14}H_{13}O_3N$ Acetylmethoxy-1-naphthaldoximes (BRADY and GOLDSTEIN), 1962.

2-Nitrodi-*p*-tolyl ether (REILLY, DRUMM, and BARRETT), 72.

3-Nitrodi-*p*-tolyl ether (REILLY and BARRETT), 1399.

$C_{14}H_{13}O_6N$ Methyl nitrocinnamylidenemalonates (BAKER and ECCLES), 2128.

$C_{14}H_{14}ON_4$ Benzophenone δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 109.

$C_{14}H_{14}O_3N_2$ Quinoxaline derivative of 2:2-dimethyl*cyclo*pentane-3:4-dione-1-carboxylic acid (GIBSON, HARIHARAN, and SIMONSEN), 3014.

$C_{14}H_{14}O_4N_2$ 2:5-Dimethoxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2340.

$C_{14}H_4O_5N_4$ 3:5-Diketo-2-*p*-tolyltetrahydro-1:2:4-triazine-6-carboxylic acid urethane (WHITELEY and YAPP), 527.

$C_{14}H_{14}NAs$ 10-Ethyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.

$C_{14}H_{15}ON$ Aminodi-*p*-tolyl ethers, and their salts (REILLY and BARRETT), 1400.

Diphenylhydroxyethylamines, and their salts (READ and STEELE), 910.

$C_{14}H_{15}N_3S$ Acetone δ-β-naphthylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2533.

$C_{14}H_{16}O_3N_2$ Nitro-9-acetylhexahydrocarbazoles (GURNEY and PLANT), 1317.

10-Nitro-7-methyl-ψ-indoxyl*spirocyclo*hexane (BETTS, MUSPRATT, and PLANT), 1313.

$C_{14}H_{16}NBr$ 2:6-Dimethylquinoline allobromine (HAMER), 2801.

$C_{14}H_{16}NI$ 2:6-Dimethylquinoline alliodide (HAMER), 2800.

$C_{14}H_{16}N_2Se_2$ Di-*o*-methylaminodiphenyl diselenide (CLARK), 2807.

$C_{14}H_{17}ON$ 9-Acetyl-*trans*-hexahydrocarbazole (GURNEY, PERKIN, and PLANT), 2679.

$C_{14}H_{17}O_2N_3$ *iso*Nitroso-derivative of substance $C_{14}H_{18}ON_2$ (KRISHNAMURTI and DEY), 1351.

$C_{14}H_{17}O_4Br_2$ Substance, from bromine and dimethylpyrone (COLLIE and KLEIN), 2162.

$C_{14}H_{17}O_6N$ Indican, synthesis of (ROBERTSON), 1937.

$C_{14}H_{17}N_2Cl$ Dibenzylhydrazine hydrochloride (KENNER and WILSON), 1112.

$C_{14}H_{18}ON_2$ Substance, from benzoylacetonitrile, piperidine, and salicylaldehyde (KRISHNAMURTI and DEY), 1350.

$C_{14}H_{18}O_2N_2$ *meso*-1:4-Diacetyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

1-*mm'*-Dimethoxyanilino-1-cyano*cyclo*pentane (OAKESHOTT and PLANT), 489.

$C_{14}H_{18}O_4N_2$ Ethyl nitropiperidinobenzoates (LE FÈVRE and TURNER), 1117.

$C_{14}H_{18}O_3N_2$ 3-Methoxy-4-ethoxystyryl methyl ketone semicarbazone (DICKINSON, HEILBRON, and IRVING), 1894.

$C_{14}H_{20}O_4N_2$ Ethyl βγ-dicyano-β-methylpentane-γε-dicarboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3011.

$C_{14}H_{22}O_8N_2$ γ-*m*-Nitro-*p*-acetamidophenylpropyltrimethylamine, picrate of (INGOLD and WILSON), 811.

$C_{14}H_{22}NI$ 4-Phenyl-1-methyl-1-ethylpiperidinium iodides (MILLS, PARKIN, and WARD), 2619.

$C_{14}H_{22}ON_2$ 2-*iso*Propylidene-β-thujone semicarbazone (HUGH and KON), 2599.

β-Thujylideneacetone semicarbazone (HUGH and KON), 2599.

$C_{14}H_{25}ON_3$ Acetone δ-*d*-bornylsemicarbazones (GOODSON), 1998.

$C_{14}H_{25}O_4Br$ Ethyl α-bromo-ββδδ′-tetramethyladipate (FARMER and KRACOVSKI), 684.

14 IV

$C_{14}H_7O_3ClS$ 4-Chloro-1:9-thionyldihydroxyanthracene (GREEN), 2344.

$C_{14}H_7O_4NCl_2$ Nitrodiphenic acid dichlorides (BELL and ROBINSON), 1697.

$C_{14}H_8O_2NCl_5$ Pentachloroacetoxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.

$C_{14}H_8O_6N_2S_2$ 3:3′-Dinitrobenzaldehyde disulphides (HODGSON and BEARD), 2423.

$C_{14}H_9O_4N_2Cl$ 2′-Chloro-2:4-dinitrostilbene (ROBINSON and ZAKI), 2489.

$C_{14}H_{10}O_3N_2Br_2$ 5:4′-Dibromo-3-nitro-4-acetamidodiphenyl (BELL and ROBINSON), 1130.

$C_{14}H_{10}O_5N_3Cl$ 3-Chloro-5:4′-dinitro-4-acetamidodiphenyl (SCARBOROUGH and WATERS), 1137.

$C_{14}H_{10}O_6N_4S_2$ Dinitrodibenzaldehyde disulphide dioximes (HODGSON and BEARD), 2424.

$C_{14}H_{10}O_7N_4Se$ Benzselenazole methopicrate (CLARK), 2806.

$C_{14}H_{10}N_4Br_2S_2$ 3-Bromo-1-aminobenzthiazole tribromide (DYSON, HUNTER, and MORRIS), 1192.

$C_{14}H_{11}ONBr_2$ 4:6-Dibromo-3-acetamidodiphenyl (BLAKEY and SCARBOROUGH), 3007.

$C_{14}H_{11}O_2NCl_2$ 3:5-Dichloro-4-methoxybenzanilide (BLAKEY, JONES, and SCARBOROUGH), 2868.

3:5-Dichloro-4-methoxybenzophenoneoxime (BLAKEY, JONES, and SCARBOROUGH), 2867.

$C_{14}H_{11}O_2N_2Br$ Phthalimidomethylpyridinium bromide (KIPPING and MANN), 530.

$C_{14}H_{11}O_3N_2Cl$ Chloronitro-4-acetamidodiphenyl (SCARBOROUGH and WATERS), 1137.

$C_{14}H_{11}O_3N_2Br$ 4-Bromo-4′-nitro-3-acetamidodiphenyl (BLAKEY and SCARBOROUGH), 3009.

4′-Bromo-3-nitro-4-acetamidodiphenyl (SCARBOROUGH and WATERS), 1139.

5-Bromo-3-nitro-4-acetamidodiphenyl (BELL and ROBINSON), 1131.

$C_{14}H_{11}O_5N_4Br$ Dinitromethoxybenzaldehyde *p*-bromophenylhydrazone (HODGSON and BEARD), 2381.

$C_{14}H_{12}ONCl$ Chloro-3-acetamidodiphenyls (BLAKEY and SCARBOROUGH), 3003.

Chloro-2-acetamidodiphenyls (SCARBOROUGH and WATERS), 93.

$C_{14}H_{12}ONBr$ 5-Bromo-2-acetamidodiphenyl (SCARBOROUGH and WATERS), 94.

Bromo-3-acetamidodiphenyls (BLAKEY and SCARBOROUGH), 3005.

$C_{14}H_{12}O_2NBr$ 3-Bromo-4-methoxybenzanilide (BLAKEY, JONES, and SCARBOROUGH), 2868.

3-Bromo-4-methoxybenzophenoneoximes (BLAKEY, JONES, and SCARBOROUGH), 2868.

$C_{14}H_{12}O_2NI$ 3-Iodo-4-methoxybenzanilide (BLAKEY, JONES, and SCARBOROUGH), 2869.

3-Iodo-4-methoxybenzophenoneoximes (BLAKEY, JONES, and SCARBOROUGH), 2869.

$C_{14}H_{12}O_2N_2Se_2$ Di-*o*-formylaminodiphenyl diselenide (CLARK), 2808.

$C_{14}H_{12}O_3N_3Cl$ 4-Chloro-2-methoxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and JENKINSON), 1741.

$C_{14}H_{12}O_3N_3Br$ Bromomethoxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 3042.

$C_{14}H_{12}O_3N_3I$ Iodomethoxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 3043.

$C_{14}H_{12}O_4NCl$ 1:3-Dihydroxy-7-methoxyxanthonimine hydrochloride (SHINODA), 1984.

Nitrochloro-2-benzyloxyanisoles (OXFORD and ROBINSON), 2241.

$C_{14}H_{13}O_4N_4S$ Nitromethylthiolbenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 2426.

$C_{14}H_{12}O_5N_2S_3$ 4-Acetamidobenzenesulphonyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{14}H_{12}NISe$ Phenylbenzselenazole methiodide (CLARK), 2807.

$C_{14}H_{13}OSAs$ 10-Ethylphenoxarsine sulphide (AESCHLIMANN), 415.

$C_{14}H_{13}O_5NS_2$ 4-Methoxytoluene-3-sulphonyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{14}H_{14}O_4N_2S$ *p*-Toluenesulphonmethyl-2-nitroanilide (BELL and ROBINSON), 1129.

$C_{14}H_{14}O_5N_2Br_2$ Ethyl diketosuccinate 2:4-dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{14}H_{15}O_2NS$ Phenylethanesulphonamides (EVANS, MABBOTT, and TURNER), 1162.

$C_{14}H_{15}NIAs$ 10:10-Dimethyl-5:10-dihydrophenarsazonium iodide (AESCHLIMANN), 416.

$C_{14}H_{15}N_2ClBr$ Di-*o*-bromobenzylhydrazine hydrochloride (KENNER and WILSON), 1111.

$C_{14}H_{16}ONBr$ 6-Bromo-9-acetylhexahydrocarbazole, and its hydrobromide (GURNEY and PLANT), 1322.

$C_{14}H_{18}O_4N_4S_2$ Carbethoxymethyl-2-glyoxaline disulphide (BALABAN and KING), 1867.

$C_{14}H_{19}O_2N_2Br$ *β*-Phthalimidodimethyldiethylammonium bromide (HANHART and INGOLD), 1010.

$C_{14}H_{19}O_2N_3S$ Acetone *S*-*o*-carbethoxybenzylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2530.

C_{15} Group.

$C_{15}H_{10}O_5$ Carajuretin, and its salts (CHAPMAN, PERKIN, and ROBINSON), 3025.

$C_{15}H_{12}O_3$ 2:4-Dihydroxyphenyl styryl ketone (ELLISON), 1723.

7-Hydroxyflavanone (ELLISON), 1722.

$C_{15}H_{12}O_4$ Acetylbenzoylpyrocatechol (GREEN), 502.

$C_{15}H_{12}O_5$ Trihydroxyphenyl hydroxystyryl ketones (ELLISON), 1723.

$C_{15}H_{12}S_2$ 2-Styryl-1:3-benzdithiole, and its nitrate (HURTLEY and SMILES), 537.

$C_{15}H_{14}O_3$ Methyl 1-methoxydiphenyl-1-carboxylate (RULE and BRETSCHER), 926.

$C_{15}H_{16}O$ Di-*o*-tolylcarbinol (BOYD and HATT), 908.

$C_{15}H_{18}O_7$ Ethyl 2:4:6-trimethoxybenzoylpyruvate (PRATT, ROBERTSON, and ROBINSON), 1983.

$C_{15}H_{22}O_3$ Dehydrongaiene dioxides (McDOWALL), 737.

$C_{15}H_{32}O_{14}$ Tetracarbomethoxy *γ*-methylfructoside (ALLPRESS, HAWORTH, and INKSTER), 1234.

$C_{15}H_{24}O_3$ Dihydrongaiol (McDOWALL), 734.

Tetrahydrongaione (McDOWALL), 733.

$C_{15}H_{22}O_2$ Tetrahydrongaiene dioxide (McDOWALL), 740.

$C_{15}H_{26}O_3$ Tetrahydrongaiol (McDOWALL), 734.

15 III

$C_{15}H_9O_3Cl$ Chlorohydroxymethylanthraquinone (HAYASHI), 2524.

$C_{15}H_9O_3Br$ Bromohydroxymethylanthraquinone (HAYASHI), 2526.

$C_{15}H_9O_5N_3$ 2:5-Dinitrophenyloxazoles (INGHAM), 698.

$C_{15}H_9O_6N_7$ 3:5-Diketo-2-*o*-nitrophenyl-6-*o*-nitrobenzeneazotetrahydro-1:2:4-triazine (WHITELEY and YAPP), 527.

$C_{15}H_{10}ON_2$ *iso*Quinazindol-2-one (ASAHINA, MANSKE, and ROBINSON), 1709.

$C_{15}H_{10}O_3N_2$ 2-Phenyl-5-*m*-nitrophenyloxazole (INGHAM), 698.

$C_{15}H_{10}O_6N_2$ 2:4-Dinitro-3':4'-methylenedioxystilbene (NISBET), 2082.

$C_{15}H_{10}N_4S$ *s*-Dicyanophenylthiocarbamides (DYSON, GEORGE, and HUNTER), 443.

$C_{15}H_{11}O_2N$ 3-Phenylindole-2-carboxylic acid (MANSKE, PERKIN, and ROBINSON), 7.

$C_{15}H_{11}O_2N_5$ 3:5-Diketo-6-benzeneazo-2-phenyltetrahydro-1:2:4-triazine (WHITELEY and YAPP), 527.

$C_{15}H_{11}O_2Cl$ 4'-Hydroxyflavylium chloride (IRVINE and ROBINSON), 2090.

$C_{15}H_{11}O_2I_3$ 4'-Hydroxyflavylium periodide (IRVINE and ROBINSON), 2090.

$C_{15}H_{11}O_3Cl$ Chrysinidin chloride (PRATT, ROBERTSON, and ROBINSON), 1977.

Dihydroxyflavylium chlorides (ROBERTSON and ROBINSON), 245, 2203.

$C_{15}H_{11}O_4Cl$ Apigenidin chloride ($+H_2O$) (PRATT, ROBERTSON, and ROBINSON), 1979.

Chlorohydroxybenzoyltoluic acids, and their salts (HAYASHI), 2520.

5:6:7-Trihydroxyflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3040.

$C_{15}H_{11}O_4Br$ Bromohydroxybenzoyltoluic acids, and their salts (HAYASHI), 2525.

$C_{15}H_{11}O_5Cl$ Resomorinidin chloride (PRATT, ROBERTSON, and ROBINSON), 1982.

5:6:7:4'-Tetrahydroxyflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3038.

$C_{11}H_{11}O_7N$ 2-Nitro-4:5-dimethoxyphenylpyruvic acid (OXFORD and RAPER), 418.

$C_{15}H_{11}O_7N_3$ 2:4:6-Trinitro-4'-methoxystilbene (NISBET), 2083.

$C_{15}H_{11}O_7Cl$ Chrysinidin perchlorate (PRATT, ROBERTSON, and ROBINSON), 1978.

$C_{15}H_{11}NS$ 1-Styrylbenzthiazole (MILLS and WHITWORTH), 2748.

$C_{15}H_{12}O_5N_2$ 2:4-Dinitro-2'-methoxystilbene (ROBINSON and ZAKI), 2489.

Nitrobenzyl-3:4-methylenedioxybenzaldoximes (BRADY and KLEIN), 880.

$C_{15}H_{13}O_2N$ Benzylidenepiperonylmethylamine, and its picrate (MALAN and ROBINSON), 2655.

$C_{15}H_{13}O_4N$ α-Phenylethyl *p*-nitrobenzoate (WARD), 453.

$C_{15}H_{13}O_5N_3$ *m*-Nitrobenzonitro-*m*-xylidides (DADSWELL and KENNER), 1107.

$C_{15}H_{13}O_5N_5$ 3-Nitro-4-acetamidobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 23.

$C_{15}H_{13}O_6N_3$ Dinitrobenzamidophenetoles (FAWCETT and ROBINSON), 2420.

Nitrobenzylnitromethoxybenzaldoximes (BRADY and KLEIN), 881.

$C_{15}H_{13}NS$ 1-β-Phenylethylbenzthiazole (MILLS and WHITWORTH), 2749.

$C_{15}H_{14}O_2N_4$ Benzil δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 110.

$C_{15}H_{14}O_3N_2$ 5-Carboxy-2-hydroxyacetophenone, and its phenylhydrazone (CHATTAWAY and PRATS), 692.

3-Nitro-4-acetmethylamidodiphenyl (BELL and ROBINSON), 1130.

m-Nitrobenzo-*m*-xylidides (DADSWELL and KENNER), 1107.

$C_{15}H_{14}O_3N_4$ *p*-Acetamidobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 22.

$C_{15}H_{14}O_4N_2$ Dinitrobenz-*p*-phenetidides (FAWCETT and ROBINSON), 2420.

Nitro-4-benzamidophenetoles (FAWCETT and ROBINSON), 2418.

Nitrobenzylmethoxybenzaldoximes (BRADY and KLEIN), 880.

$C_{15}H_{14}O_6N_2$ Nitro-3-methoxy-4-*p*-nitrobenzyloxytoluenes (OXFORD), 1967.
$C_{15}H_{15}N_3S$ Benzylidenebenzylthiosemicarbazide (BAIRD, BURNS, and WILSON), 2581.
$C_{15}H_{17}O_3N$ 7-Acetyl-ψ-indoxyl*spirocyclo*hexane (BETTS, MUSPRATT, and PLANT), 1312.
$C_{15}H_{17}O_8N$ 3-β-Glucosidoxyindole-2-carboxylic acid (ROBERTSON), 1940.
$C_{15}H_{17}O_8N_5$ Mesoxalyldiurethane nitrophenylhydrazones (WHITELEY and YAPP), 525.
$C_{15}H_{17}O_3N_2$ Substance, from *o*-phenylenediamine and α-keto-ββγγ-tetramethylglutaric hydroxylactone (ROTHSTEIN and SHOPPEE), 534.
$C_{15}H_{18}O_5N_2$ Ethyl diketosuccinate tolylhydrazones (CHATTAWAY and HUMPHREY), 2795.
$C_{15}H_{18}O_6N_4$ Mesoxalyldiurethane phenylhydrazone (WHITELEY and YAPP), 525.
$C_{15}H_{18}O_7N_2$ 3-β-Glucosidoxyindole-2-carboxylamide (ROBERTSON), 1940.
$C_{15}H_{23}O_2Cl$ Ngaiyl chloride, preparation of (MCDOWALL), 739.
$C_{15}H_{23}N_3S$ Benzylidene-5-heptylthiosemicarbazide (BAIRD, BURNS, and WILSON), 2534.
$C_{15}H_{24}NI$ 4-Phenyl-1:1-diethylpiperidinium iodide (MILLS, PARKIN, and WARD), 2621.
$C_{15}H_{25}ON_3$ Methyl-β-thujylideneacetone semicarbazone (HUGH and KON), 2599.
$C_{15}H_{25}O_2N$ Ngaiylamine, and its salts (MCDOWALL), 738.
$C_{15}H_{28}O_2N_2$ Tetrahydrongaione hydrazone (MCDOWALL), 736.
$C_{15}H_{29}O_2N$ Tetrahydrongaiylamine, and its picrolonate (MCDOWALL), 734.

15 IV

$C_{15}H_{12}O_4N_2S$ *s*-Di-*o*-carboxyphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.
$C_{15}H_{13}O_6N_3S$ *m*-Nitrophenyl β-(*p*-nitrobenzoyl)oxyethyl sulphide (BENNETT and BERRY), 1669.
$C_{15}H_{13}ONS$ *o*-Cinnamamidothiophenol (MILLS and WHITWORTH), 2746.
4-Keto-2-phenyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2745.
$C_{15}H_{13}O_2NS$ 2-Keto-2-phenyltetrahydro-1:5-heptabenzthiazine sulphoxide (MILLS and WHITWORTH), 2745.
$C_{15}H_{13}O_2N_3Br_2$ *o*-Acetamidobenzoyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 331.
$C_{15}H_{13}O_3NS$ 4-Keto-2-phenyltetrahydro-1:5-heptabenzthiazine sulphone (MILLS and WHITWORTH), 2746.
$C_{15}H_{13}O_3N_3Br$ Nitrobenzoylbromoacetoxylidides (DADSWELL and KENNER), 1106.
$C_{15}H_{14}ONAs$ 5-Acetyl-10-methyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.
$C_{15}H_{14}O_3BrAs$ 10-Methyl-10-carboxymethylphenoxarsonium bromide (AESCHLIMANN), 415.
$C_{15}H_{15}O_4NS_2$ *m*-Carboxyphenylmethylsulphine-*p*-toluenesulphonylimine, resolution of, and its salts (CLARKE, KENYON, and PHILLIPS), 188.
$C_{15}H_{16}O_2N_2S$ *s*-Dianisylthiocarbamides (DYSON, GEORGE, and HUNTER), 440.
$C_{15}H_{17}O_2N_2Cl$ *o*-Nitrobenzylphenyldimethylammonium chloride (BAW), 1398.
$C_{15}H_{17}NIAs$ 10-Methyl-10-ethyl-5:10-dihydrophenarsazonium iodide (AESCHLIMANN), 416.

C_{16} Group.

$C_{16}H_{10}O_4$ 4-Hydroxy-3-benzoylcoumarin (HEILBRON and HILL), 1707.
$C_{16}H_{12}O_2$ 7-Hydroxy-2-phenyl-5-methylbenzopyrylium anhydro-base, and its salts (HIRST), 2493.
$C_{16}H_{12}O_3$ 4-Hydroxy-3-benzylcoumarin (HEILBRON and HILL), 1707.

$C_{16}H_{12}O_5$ Carajurone (CHAPMAN, PERKIN, and ROBINSON), 3027.
$C_{16}H_{12}N_2$ Dibenzodihydronaphthyridine, and its salts (HAWORTH and PINK), 2348.
$C_{16}H_{14}O$ *o-iso*Propenylbenzophenone (BARNETT, COOK, and NIXON), 509.
$C_{16}H_{14}O_3$ Phenyl 2-hydroxy-5-methoxystyryl ketone (IRVINE and ROBINSON), 2088.
$C_{16}H_{14}O_4$ 2:2′-Dimethoxybenzil, surface tension and density of (GARNER and SUGDEN), 2882.
$C_{16}H_{15}N$ 1-Benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its sulphate (CHAKRAVARTI, HAWORTH, and PERKIN), 2277.
$C_{16}H_{16}O_2$ Dimethylphenylhydroxyphthalan (BARNETT, COOK, and NIXON), 509.
2-*p*-Tolyloxy-5-methylacetophenone (REILLY and DRUMM), 2819.
$C_{16}H_{21}N_3$ 2-Aminotetramethylbenzidine (BELL and ROBINSON), 1698.
$C_{16}H_{22}O_5$ Ethyl β-benzyloxyethylmalonate (BENNETT and HOCK), 475.
$C_{16}H_{26}O_6$ Tetramethylmannonic acid phenylhydrazide (GOODYEAR and HAWORTH), 3143.
$C_{16}H_{32}O_2$ Palmitic acid, sodium salt, effect of electrolytes on viscosity of (MCBAIN, WILLAVOYS, and HEIGHINGTON), 2689; hydrolysis of solutions of (MCBAIN and BUCKINGHAM), 2679.
Acid, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1900.

16 III

$C_{16}H_9O_2Cl$ 2-*o*-Chlorobenzylidene-1:3-diketohydrindene (ROBINSON and ZAKI), 2488.
$C_{16}H_{10}ON_2$ Ketodibenzodihydronaphthyridine, and its salts (HAWORTH and PINK), 2347.
$C_{16}H_{10}O_4N_2$ *o*-Nitrobenzylidenehomophthalimide (HAWORTH and PINK), 2346.
$C_{16}H_{10}O_5N_4$ 3-Keto-2:5-dinitrophenyl-3:4-dihydro-1:4-diazines (INGHAM), 699.
$C_{16}H_{12}O_{12}N_6$ 1:4-Di-*oop*-trinitrophenylpiperazine (LE FÈVRE and TURNER), 1121.
$C_{16}H_{13}ON$ 2-Acetyl-3-phenylindole (MANSKE, PERKIN, and ROBINSON), 8.
$C_{16}H_{13}O_2Cl$ Methoxyflavylium chlorides (IRVINE and ROBINSON), 2088.
$C_{16}H_{13}O_5Cl$ Hydroxymethoxyflavylium chlorides (IRVINE and ROBINSON), 2091.
Scutellareinidin chloride methyl ether (CHAPMAN, PERKIN, and ROBINSON), 3038.
5:6:7:4′-Tetrahydroxy-4-methylflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3035.
$C_{16}H_{13}O_6Cl$ Rhamnetinidin chloride (ROBERTSON and ROBINSON), 2206.
$C_{16}H_{14}ON_2$ Ketodibenzohexahydronaphthyridine, and its salts (HAWORTH and PINK), 2348.
$C_{16}H_{14}O_3N_2$ Nitrobenzylcinnamaldoximes (BRADY and KLEIN), 879.
$C_{16}H_{14}O_6N_4$ Ethyl 2:4-dinitrobenzoylformate phenylhydrazone (FAIRBOURNE and FAWSON), 49.
$C_{16}H_{14}O_6Cu$ Cuprimandelic acid, salts of (WARK), 1755.
$C_{16}H_{14}O_8N_6$ 1:4-Di-*op*-dinitrophenylpiperazine (LE FÈVRE and TURNER), 1121.
$C_{16}H_{15}O_2N$ Diacetyl-4-aminodiphenyl (SCARBOROUGH and WATERS), 1139.
$C_{16}H_{15}O_3N_3$ α-Phenylbutane-βγ-dione β-*m*-nitrophenylhydrazone (MANSKE, PERKIN, and ROBINSON), 7.
$C_{16}H_{15}O_4N_3$ 2:4-Dinitro-4′-dimethylaminostilbene, and its chloroplatinate (NISBET), 2083.
$C_{16}H_{15}O_6N_3$ Methyl *pp*′-dinitrodibenzylaminoformate (BAKER), 568.
$C_{16}H_{16}ON_2$ *p*-Acetamidobenzylidene-*p*-toluidine (HODGSON and BEARD), 22.
α-Phenylbutane-βγ-dione β-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 7.
$C_{16}H_{16}ON_4$ Benzaldehyde acetophenone carbohydrazone (BROWN, PICKERING, and WILSON), 109.

$C_{16}H_{16}O_2N_4$ Di-*p*-tolylformazylcarboxylic acid (WHITELEY and YAPP), 526.
$C_{16}H_{17}O_2N$ Methyl dibenzylaminoformate (BAKER), 568.
$C_{16}H_{17}O_3N$ *N*-*o*-Methoxybenzyl-*p*-methoxybenzaldoxime (BRADY and BENNETT), 896.
$C_{16}H_{17}N_3S$ Acetophenone δ-benzylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2531.
Benzylidene-δ-α-phenylethylthiosemicarbazide (BAIRD, BURNS, and WILSON), 2532.
Dibenzyl ketone thiosemicarbazone (BAIRD and WILSON), 2117.
$C_{16}H_{18}O_4N_2$ Bisnitrosyl-*o*-methoxybenzyl (BRADY and BENNETT), 897.
$C_{16}H_{18}N_2Br_2$ Dibromohexadiene dipyridinium salt (FARMER, LAROIA, SWITZ, and THORPE), 2950.
$C_{16}H_{19}ON$ β-Amino-α-ethyl-αβ-diphenylethyl alcohol, and its hydrochloride (MCKENZIE and ROGER), 576.
$C_{16}H_{20}OSi$ Diethoxydiphenylsilicane (KIPPING and MURRAY), 2736.
$C_{16}H_{20}O_2N_2$ Acetamido-9-acetylhexahydrocarbazoles (GURNEY and PLANT), 1317.
$C_{16}H_{20}O_6N_4$ Mesoxalyldiurethane *p*-tolylhydrazone (WHITELEY and YAPP), 525.
$C_{16}H_{20}NCl$ Phenyl-α-phenylethyldimethylammonium chloride (EVANS, MABBOTT, and TURNER), 1163.
$C_{16}H_{22}ON_2$ Pinene nitrolanilide (EARL and KENNER), 1275.
$C_{16}H_{22}O_4N_4$ 4:6-Dinitro-1:3-dipiperidinobenzene (LE FÈVRE and TURNER), 1118.
$C_{16}H_{23}O_2N_3$ 1-Nitro-2:4-dipiperidinobenzene (LE FÈVRE and TURNER), 1117.
$C_{16}H_{23}O_3N$ Tetramethyladipanilic acids (FARMER and KRACOVSKI), 683.
$C_{16}H_{24}O_3S$ Menthyl benzenesulphonate, decomposition and rotation of (PATTERSON and MCALPINE), 350.
$C_{16}H_{26}O_6N_2$ Tetramethyl δ-galactonolactone phenylhydrazide (HAWORTH, HIRST, and JONES), 2430.
Tetramethyl mannonophenylhydrazide (DREW, GOODYEAR, and HAWORTH), 1243.

16 IV

$C_{16}H_8O_2N_4Cl_4$ Anhydrodiketosuccinic acid 2:4-dichlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.
Dichlorophenyl-4:5-diketopyrazoline-3-carboxylic acid dichlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.
$C_{16}H_8O_2N_4Br_4$ Anhydrodiketosuccinic acid 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1325.
1-2′:4′-Dibromophenyl-4:5-diketopyrazoline-3-carboxylic acid 4-2″:4″-dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1325.
$C_{16}H_{10}O_2N_4Cl_2$ Anhydrodiketosuccinic acid chlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.
Chlorophenyl-4:5-diketopyrazoline-3-carboxylic acid chlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1328.
$C_{16}H_{10}O_2N_4Br_2$ Anhydrodiketosuccinic acid *p*-bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.
1-*p*-Bromophenyl-4:5-diketopyrazoline-3-carboxylic acid 4-*p*-bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.
$C_{16}H_{10}O_4N_4Cl_4$ Diketosuccinic acid 2:4-dichlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.
$C_{16}H_{10}O_4N_4Br_4$ Diketosuccinic acid 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1325.
$C_{16}H_{11}O_3N_4Br$ 1-Phenyl-4:5-diketopyrazoline-3-carboxylic acid 4-bromophenylhydrazone (CHATTAWAY and HUMPHREY), 2138.
$C_{16}H_{11}NClAs$ 7-Chloro-7:12-dihydro*iso*benzophenarsazine (GIBSON and JOHNSON), 2513.

$C_{16}H_{11}NBrAs$ 12-Bromo-7:12-dihydrobenzophenarsazine (GIBSON and JOHNSON), 2513.

$C_{16}H_{12}O_2NHS$ Benzophenarsazinic acids, and their salts (GIBSON and JOHNSON), 2511.

$C_{16}H_{12}O_4N_4Cl_2$ Diketosuccinic acid *p*-chlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_{12}O_4N_4Br_2$ Diketosuccinic acid *p*-bromophenylosazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_{13}O_5N_2As$ Benzoyloxy-1:4-dihydroquinoxaline-6-arsinic acids (EWINS, NEWBERY, and STICKINGS), 853.

$C_{16}H_{14}O_2N_2Br_2$ Succino-*p*-bromoanilide (BARNICOAT), 2928.

$C_{16}H_{14}O_3NBr$ Benzoyl-6-bromo-β-piperonylethylamine (STEVENS), 184.

$C_{16}H_{14}O_3NAs$ 2-Naphthylaminophenylarsinic acids (GIBSON and JOHNSON), 2511.

$C_{16}H_{15}O_4N_4Br$ Substance, from piperazine and 4:4′-dibromo-3:2′-dinitrodiphenyl (LE FÈVRE and TURNER), 1121.

$C_{16}H_{16}O_2N_2Se_2$ Di-*o*-formylmethylaminodiphenyl diselenide (CLARK), 2806.

$C_{16}H_{16}N_4Br_6S_2$ 1-Amino-5-methylbenzthiazole tribromide (DYSON, HUNTER, and MORRIS), 1192.

$C_{16}H_{18}O_4N_3Cl$ Di-*p*-nitrobenzyldimethylammonium chloride (STEDMAN), 1905.

$C_{16}H_{20}O_3NCl$ Chlorocamphoranilic acids (M. and R. SINGH), 1995.

$C_{16}H_{25}O_{12}N_3Co$ Aquo-2:6-dinitrophenoxobisethylenediamminocobaltic hydroxy-2:6-dinitrophenoxide (DUFF and BILLS), 2374.

16 V

$C_{16}H_{10}O_6N_2S_2Na_2$ Sodium *p*-sulphobenzeneazo-β-naphthyl sulphite (KING), 2644.

$C_{16}H_{11}O_4NCl_6S$ Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene-5-sulphonanilide (CHATTAWAY and MORRIS), 2017.

C_{17} Group.

$C_{17}H_{10}O_4$ *iso*Benzanthragallol (CROSS and PERKIN), 1303.

Benzanthrapurpurin (CROSS and PERKIN), 1302.

*iso*Benzflavopurpurin (CROSS and BEVAN), 1305.

$C_{17}H_{12}O_4$ α-(6-Hydroxymethylpiperonyl)cinnamolactone (STEVENS and ROBERTSON), 2791.

$C_{17}H_{14}O$ Carajurin, and its salts (CHAPMAN, PERKIN, and ROBINSON), 3023.

$C_{17}H_{14}O_4$ 7-Acetoxyflavanone (ELLISON), 1722.

$C_{17}H_{14}O_5$ 3-(3′:4′-Dihydroxybenzylidene)-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 2097.

$C_{17}H_{16}O_2$ 1-Acetonyl-3-methyl-1:4-β-naphthapyran (DICKINSON and HEILBRON), 17.

7-Methoxy-2-phenyl-5-methylbenzopyrylium hydroxide, ferrichloride of (HIRST), 2494.

$C_{17}H_{16}O_3$ Phenyl 3:4-dimethoxystyryl ketone (DICKINSON, HEILBRON, and IRVING), 1896.

1:2:7-Trimethoxyanthracene (MACMASTER and PERKIN), 1309.

$C_{17}H_{16}O_4$ 3:4:6-Trimethoxyanthranol (MACMASTER and PERKIN), 1309.

$C_{17}H_{16}O_5$ 3-(3′:4′-Dihydroxybenzyl)-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 2098.

Phenacyl veratrate (MALAN and ROBINSON), 2656.

$C_{17}H_{17}N$ Tetrahydroprotoberberine, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2278.

$C_{17}H_{17}N_3$ 5-Keto-6-phenyl-2:3:4:5-tetrahydropyridine 5-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 10.

$C_{17}H_{21}N$ Benzyl-*n*-butylaniline, and its salts (REILLY and DRUMM), 1895.[A]

$C_{17}H_{22}O_7$ Methyl ethyl hydrogen 4-methyl-5-*cyclo*hexane*spiro*-Δ^1-*cyclo*penten-3-one-1:2:4-tricarboxylate (INGOLD and SEELEY), 1688.

$C_{17}H_{22}N_2$ Benzyl-*n*-butyl-*p*-phenylenediamine, and its salts (REILLY and DRUMM), 1396.

$C_{17}H_{26}O_9$ Ethyl $\beta\delta$-dicarbethoxy-γ-ketopimelate (ROBINSON and ZAKI), 2413.

$C_{17}H_{30}O_4$ Tetrahydrongaiol acetate (MCDOWALL), 734.

17 III

$C_{17}H_{10}OS_2$ 1:3-Benzdithiole-2-β-naphthaquinone, and its hydrochloride (HURTLEY and SMILES), 536.

$C_{17}H_{11}O_4N_3$ 3-Nitrobenzaldehyde-4-azo-β-naphthol (HODGSON and BEARD), 23.

$C_{17}H_{12}O_2N_4$ 2:6-Dibenzeneazopyrone (MULLEN and CROWE), 1752.

$C_{17}H_{12}O_5Br$ Dibromocarajurin (CHAPMAN, PERKIN, and ROBINSON), 3024.

$C_{17}H_{13}ON$ Oxyprotoberberine (CHAKRAVARTI, HAWORTH, and PERKIN), 2279.

$C_{17}H_{13}O_2Cl$ Chlorohydroxydistyryl ketones (HEILBRON and HILL), 921.

$C_{17}H_{14}O_3N_4$ Methyl 1-phenyl-4:5-diketopyrazoline-3-carboxylate 4-phenylhydrazone (CHATTAWAY and HUMPHREY), 2139.

$C_{17}H_{14}O_5Br_4$ Carajurin tetrabromide (CHAPMAN, PERKIN, and ROBINSON), 3023.

$C_{17}H_{14}NCl$ Protoberberinium chloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2279.

$C_{17}H_{14}NI$ Protoberberinium iodide (CHAKRAVARTI, HAWORTH, and PERKIN), 2279.

$C_{17}H_{15}O_2Cl$ 7-Methoxy-2-phenyl-5-methylbenzopyrylium chloride (HIRST), 2494.

$C_{17}H_{15}O_2N$ Ethyl 3-phenylindole-2-carboxylate (MANSKE, PERKIN, and ROBINSON), 7.

$C_{17}H_{15}O_2N_5$ 3:5-Diketo-6-*p*-tolueneazo-2-*p*-tolyltetrahydro-1:2:4-triazine (WHITELEY and YAPP), 527.

$C_{17}H_{15}O_3Cl$ 3:4′-Dimethoxyflavylium chloride (ROBERTSON and ROBINSON), 2203.

7-Hydroxy-4′-methoxy-2-phenyl-5-methylbenzopyrylium chloride (HIRST), 2494.

$C_{17}H_{15}O_4Cl$ 3:5:4′-Trihydroxy-6:8-dimethylflavylium chloride (ROBERTSON and ROBINSON), 2204.

$C_{17}H_{15}O_5Cl$ 5:7-Dihydroxy-3′:4′-dimethoxyflavylium chloride (PRATT, ROBERTSON, and ROBINSON), 1981.

5:7-Dihydroxy-6:4′-dimethoxyflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3039.

3:5:3′:4′-Tetrahydroxy-6:8-dimethylflavylium chloride (ROBERTSON and ROBINSON), 2205.

$C_{17}H_{15}O_7N_7$ Di-*o*-nitroformazylcarboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{17}H_{17}O_3N_3$ *meso*-1-*p*-Nitrobenzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

$C_{17}H_{17}O_3N_5$ Formazylcarboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{17}H_{17}O_4N$ Piperonylmethyl-β-piperonylethylamine (MALAN and ROBINSON), 2656.

$C_{17}H_{17}O_6N_3$ 2-Nitro-4:5-dimethoxyphenylpyruvic acid phenylhydrazone (OXFORD and RAPER), 419.

$C_{17}H_{18}ON_2$ 1-Benzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxalines (GIBSON), 344.

$C_{17}H_{18}ON_4$ Diacetophenonecarbohydrazone (BROWN, PICKERING, and WILSON), 109.

$C_{17}H_{18}O_3N_2$ 5-Piperidino-2-nitrodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1171.

$C_{17}H_{18}O_4N_4$ 4:6-Dinitro-3-anilino-1-piperidinobenzene (LE FÈVRE and TURNER), 1118.

$C_{17}H_{19}O_3N_3$ 4-Nitro-2-benzylideneaminodiethylaniline (BURTON and GIBSON), 2388.

$C_{17}H_{19}O_3N$ 2:6-Dimethoxy-4-methylbenz-*p*-toluidide (ROBERTSON and ROBINSON), 2200.

$C_{17}H_{19}O_3N_3$ Phenyl *β*-2-hydroxy-5-methoxyphenylethyl ketone semicarbazone (IRVINE and ROBINSON), 2093.

$C_{17}H_{19}O_5N$ Ethyl *δ*-phthalimido-*α*-acetylvalerate (MANSKE, PERKIN, and ROBINSON), 8.

$C_{17}H_{20}ON_2$ *p*-Nitrosobenzyl-*n*-butylaniline, and its hydrochloride (REILLY and DRUMM), 1396.

$C_{17}H_{20}N_2S$ *s*-Di-*m*-xylyl-2-thiocarbamide (DYSON, GEORGE, and HUNTER), 440.

$C_{17}H_{23}ON$ *α*-Ethyl-Δ^1-*cyclo*hexenylacet-*p*-toluidide (KON and NARAYANAN), 1540.

$C_{17}H_{28}NI$ 4-Phenyl-1:1-di-*n*-propylpiperidinium iodide (MILLS, PERKIN, and WARD), 2622.

17 IV

$C_{17}H_{10}O_3N_4Br_4$ Methyl 1-2′:4′-dibromophenyl-4:5-diketopyrazoline-3-carboxylate dibromophenyl hydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{17}H_{12}O_3N_4Br_2$ Methyl 1-*p*-bromophenyl-4:5-diketopyrazoline-3-carboxylate bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{17}H_{12}O_9N_2S_2$ Nitrobenzoylnaphthylaminedisulphonic acids, and their sodium salts (BALABAN and KING), 3078.

$C_{17}H_{12}O_{10}N_2S_2$ Nitrobenzoylamino-8-naphthol-3:6-disulphonic acids, salts (BALABAN and KING), 3090.

$C_{17}H_{13}O_{12}N_2S_3$ *m*-Nitrobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, salts (BALABAN and KING), 3095.

$C_{17}H_{14}O_4NBr$ Piperonylidene-6-bromo-*β*-piperonylethylamine (STEVENS), 184.

$C_{17}H_{14}O_7N_2S_2$ Aminobenzoylnaphthylaminedisulphonic acids, and their salts (BALABAN and KING), 3079.

$C_{17}H_{14}O_8N_2S_2$ *m*-Aminobenzoylamino-8-naphthol-3:6-disulphonic acids, and their salts (BALABAN and KING), 3090.

$C_{17}H_{15}O_2NS$ Acetyl-4-keto-2-phenyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2745.

$C_{17}H_{15}O_3N_2Br_2$ *o*-Acetamidobenzoyl-*α*-acetyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 331.

$C_{17}H_{15}O_6N_4Br$ 4-Bromo-2:3′:5′-trinitro-4′-piperidinodiphenyl (LE FÈVRE, MOIR, and TURNER), 2338.

$C_{17}H_{16}O_2N_2Br_2$ Glutaro-*p*-bromoanilide (BARNICOAT), 2928.

$C_{17}H_{16}O_2N_2S$ *s*-Di-*p*-acetylphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 442.

$C_{17}H_{16}O_3NBr$ Benzoylmethylbromopiperonylethylamine (STEVENS), 185.

$C_{17}H_{18}O_2N_4S$ *s*-Di-*p*-acetamidophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.

$C_{17}H_{20}O_2N_2S$ *s*-Diethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.

1-*p*-Toluenesulphonyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxalines (GIBSON), 345.

$C_{17}H_{20}O_4N_2S$ *s*-Bisdimethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.

C_{18} Group.

$C_{18}H_{12}As_2$ Tri-*o*-phenylenediarsine (MCCLELAND and WHITWORTH), 2753.

$C_{18}H_{14}O_4$ Diacetoxyanthracenes (GREEN), 556.

ββ′-Diphenylmuconic acid (FARMER and DUFFIN), 411.

$C_{18}H_{14}O_6$ Diacetylflavopurpurin-anthranol (CROSS and PERKIN), 1304.

$C_{18}H_{16}O_2$ 4-Phenacyl-2-methyl-1:4-benzopyran (HEILBRON and HILL), 924.

$C_{18}H_{16}O_4$ *ββ′*-Diphenyl-$\Delta\beta$-dihydromuconic acids (FARMER and DUFFIN), 412.

$C_{18}H_{16}Br_2$ Dibromo-*αζ*-diphenylhexadiene (FARMER, LAROIA, SWITZ, and THORPE), 2955.

$C_{18}H_{16}Br_4$ Tetrabromo-$a\zeta$-diphenylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2956.

$C_{18}H_{16}Br_6$ Hexabromo-$a\zeta$-diphenylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2956.

$C_{18}H_{18}O_3$ 3-Methoxy-4-benzyloxystyryl methyl ketone (DICKINSON, HEILBRON, and IRVING), 1895.

$C_{18}H_{18}O_4$ *p*-Anisyl 4-hydroxy-2-methoxy-6-methylstyryl ketone (HIRST), 2495.

3:4:6:9-Tetramethoxyanthranol (MACMASTER and PERKIN), 1308.

$C_{18}H_{19}N$ Anhydromethyltetrahydroprotoberberine, and its hydrochloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2280.

$C_{18}H_{20}O_2$ Diethylphenylhydroxyphthalan (BARNETT, COOK, and NIXON), 510.

$C_{18}H_{23}N$ Di(β-phenylethyl)dimethylamine, picrate of (HANHART and INGOLD), 1009.

$C_{18}H_{28}O_8$ Ethyl 2:3-dimethyl*cyclo*butane-1:1:4:4-tetracarboxylate (VOGEL), 1991.

$C_{18}H_{30}O_8$ Ethyl $\beta\gamma$-dimethylbutane-$a\alpha\delta\delta$-tetracarboxylate (VOGEL), 1990.

$C_{18}H_{32}O_{16}$ Melezitose (LEITCH), 588.

$C_{18}H_{34}O_2$ Oleic acid, potassium hydrogen salt, crystalline (MCBAIN and STEWART), 1392.

18 III

$C_{18}H_{13}O_2AS_2$ Tri-*o*-phenylenediarsine oxide (MCCLELAND and WHITWORTH), 2755.

$C_{18}H_{13}Br_4AS_2$ Tri-*o*-phenylenediarsine tetrabromide (MCCLELAND and WHITWORTH), 2755.

$C_{18}H_{13}ON_3$ Rutæcarpine, synthesis of (ASAHINA, MANSKE, and ROBINSON), 1708.

$C_{18}H_{13}OAS$ 10-Phenylphenoxarsine (AESCHLIMANN), 415.

$C_{18}H_{13}O_2AS$ 10-Phenylphenoxarsine oxide (AESCHLIMANN), 415.

$C_{18}H_{13}O_4Cl$ 4-Chloro-1:9-diacetoxyanthracene (GREEN), 2343.

$C_{18}H_{14}NAS$ 10-Phenyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.

$C_{18}H_{15}O_2Cl$ 4′-Chloro-2-methoxydistyryl ketone (HEILBRON and HILL), 923.

$C_{18}H_{15}O_4N$ 6:7-Methylenedioxy-2-piperonylmethyl-3:4-dihydro*iso*quinolinium hydroxide, picrate of (MALAN and ROBINSON), 2656.

$C_{18}H_{18}O_3N_4$ Anhydrodiketosuccinic acid tolylosazones (CHATTAWAY and HUMPHREY), 2795.

4:5-Diketo-1-tolylpyrazolinecarboxylic acid tolylhydrazones (CHATTAWAY and HUMPHREY), 2795.

$C_{18}H_{16}O_4AS_2$ Phenylene-1:2-diphenylarsinic acid (MCCLELAND and WHITWORTH), 2754.

$C_{18}H_{17}O_3Cl$ 4′:7-Dimethoxy-2-phenyl-5-methylbenzopyrylium chloride (HIRST), 2494.

$C_{18}H_{17}O_4Cl$ 5:6:7-Trimethoxyflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3040.

$C_{18}H_{17}O_5Cl$ 5:7-Dihydroxy-6:4′-dimethoxy-4-methylflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3034.

7-Hydroxy-3:2′:4′-trimethoxyflavylium chloride (PRATT, ROBERTSON, and ROBINSON), 1982.

$C_{18}H_{17}O_5N$ *N*-Formylpiperonylmethyl-β-piperonylethylamine (MALAN and ROBINSON), 2656.

$C_{18}H_{18}O_4N_4$ Diketosuccinic acid tolylosazones (CHATTAWAY and HUMPHREY), 2795.

$C_{18}H_{19}O_3N$ 6-Methoxy-1-(3′-methoxybenzyl)-3:4-dihydro*iso*quinoline, and its picrate (CHAKRAVARTI, HAWORTH, and PERKIN), 2270.

$C_{18}H_{20}O_2N_6$ Diacetophenonehydrazidicarbohydrazone (BROWN, PICKERING, and WILSON), 111.

Dibenzoyl derivative of β-methyltrimethylenediamine (MANN), 2916.

$C_{18}H_{20}O_3N_2$ α-Phenylbutane-βγ-dione β-2:5-dimethoxyphenylhydrazone (MANSKE, PERKIN, and ROBINSON), 7.

$C_{18}H_{20}O_4N_2$ 4-Methoxy-*m*-oxalotoluidide (DADSWELL and KENNER), 585.

$C_{18}H_{20}NI$ Tetrahydroprotoberberine methiodides (CHAKRAVARTI, HAWORTH, and PERKIN), 2280.

$C_{18}H_{21}O_2N$ 6-Methoxy-1-(3′-methoxybenzyl)-1:2:3:4-tetrahydro*iso*quinoline, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2270.

$C_{18}H_{21}O_4N_3$ Diacetyl derivative of substance $C_{14}H_{18}ON_2$ (KRISHNAMURTI and DEY), 1351.

$C_{18}H_{23}ON$ β-Thujylideneacetanilide (HUGH and KON), 2598.

$C_{18}H_{31}ON_3$ Methyl*cyclo*hexanone δ-*d*-bornylsemicarbazones (GOODSON), 1999.

18 IV

$C_{18}H_{12}O_3N_4Cl_4$ Ethyl dichlorophenyldiketopyrazoline-3-carboxylate dichlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{18}H_{12}O_3N_4Br_4$ Ethyl dibromophenyl-4:5-diketopyrazoline-3-carboxylate dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{18}H_{15}OClSi$ Phenoxydiphenylsilicyl chloride, and its action with sodium (KIPPING), 2728.

$C_{18}H_{14}O_3N_4Cl_2$ Ethyl chlorophenyl-4:5-diketopyrazoline-3-carboxylate chlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1328.

$C_{18}H_{14}O_3N_4Br_2$ Ethyl 1-*p*-bromophenyl-4:5-diketopyrazoline-3-carboxylate bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{18}H_{16}O_4NBr$ 6:7-Methylenedioxy-2-piperonylmethyl-3:4-dihydro*iso*quinolinium bromide (MALAN and ROBINSON), 2656.

$C_{18}H_{18}O_2N_2Br_2$ Adipo-*p*-bromoanilide (BARNICOAT), 2928.

$C_{18}H_{18}O_2N_2S$ Benzaldehyde *S*-*o*-carbethoxybenzylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2530.

$C_{18}H_{20}O_2N_2S$ Thiodipropiondianilide (BENNETT and SCORAH), 196.

$C_{18}H_{20}O_6N_2As$ 3-*m*-Nitrobenzamido-4-piperidinophenylarsinic acid, and its salts (KING), 1054.

$C_{18}H_{22}O_4N_3As$ 3-*m*-Aminobenzamido-4-piperidinophenylarsinic acid, and its salts (KING), 1054.

$C_{18}H_{32}O_{16}N_{11}Co$ Aquopentamminocobaltic dinitrophenoxides (DUFF and BILLS), 2370.

$C_{18}H_{27}O_9N_8Co$ *p*-Nitrophenoxopentamminocobaltic *p*-nitrophenoxide (DUFF and BILLS), 2370.

18 V

$C_{18}H_{18}ON_2Cl_5Mo$ Diquinolinium molybdenyl pentachloride (JAMES and WARDLAW), 2148.

C_{19} Group.

$C_{19}H_{14}O_3$ 2-Phenyl-5-methyl-3:4-ceumalo-6-benzopyran (HEILBRON and HILL), 924.

$C_{19}H_{14}O_4$ *iso*Benzanthragallol dimethyl ether (CROSS and PERKIN), 1303.
*iso*Benzflavopurpurin dimethyl ether (CROSS and BEVAN), 1306.

$C_{19}H_{16}O$ Benzhydryl phenyl ether (HEILBRON and HILL), 2011.

$C_{19}H_{18}O_5$ 9-Acetyl-3:4:6-trimethoxyanthranol (MACMASTER and PERKIN), 1309.

$C_{19}H_{18}O_7$ Quercetin tetramethyl ether (ATTREE and PERKIN), 239.

$C_{19}H_{20}O_5$ 3-Homoveratryl-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 2098.

$C_{19}H_{28}O_3$ Benzoyl-5-acetyl-1:3:3:4:4-pentamethyl*cyclo*pentan-1-ol (VOGEL), 599.

$C_{19}H_{30}O_{14}$ Tetracarbethoxymethylfructosides (ALLPRESS, HAWORTH, and INKSTER), 1235.

19 III

$C_{19}H_{14}O_3N_2$ Benzoyl-*o*-nitrodiphenylamine (CHAPMAN), 1748.
p-Nitrobenzoyldiphenylamine (CHAPMAN), 1749.
N-Phenylbenzimino-*p*-nitrophenyl ether (CHAPMAN), 1745.

$C_{19}H_{15}O_2N_3$ Benzenyl-*p*-nitrodiphenylamidine (CHEW and PYMAN), 2320.

$C_{19}H_{16}OS$ Dibenzylidenepenthianone (BENNETT and SCORAH), 199.

$C_{19}H_{16}O_3N_4$ 3:5-Dibenzeneazo-2:6-dimethylpyrone (MULLEN and CROWE), 1753.

$C_{19}H_{16}O_4N_2$ 6:7-Methylenedioxy-1-cyano-2-piperonylmethyl-1:2:3:4-tetrahydro*iso*quinoline (MALAN and ROBINSON), 2657.

$C_{19}H_{17}O_3N$ 3:11-Dimethoxyoxyprotoberberine (CHAKRAVARTI, HAWORTH, and PERKIN), 2273.

$C_{19}H_{17}O_4N_3$ Ethyl 1-phenyl-4-benzamido-5-ketopyrazoline-3-carboxylate (CHATTAWAY and HUMPHREY), 2136.

$C_{19}H_{18}O_3N_2$ 6-Nitro-9-benzoylhexahydrocarbazole (GURNEY and PLANT), 1321.

$C_{19}H_{18}O_5N_4$ *n*-Propyl 1-phenyl-4:5-diketopyrazoline-3-carboxylate 4-phenylhydrazone (CHATTAWAY and HUMPHREY), 2139.

$C_{19}H_{18}O_5Br_2$ Veratrylidene-7-methoxychromanone dibromide (PERKIN, RÂY, and ROBINSON), 2097.

$C_{19}H_{18}O_6N_2$ 6:7-Methylenedioxy-1-nitromethyl-2-piperonylmethyl-1:2:3:4-tetrahydro*iso*quinoline (MALAN and ROBINSON), 2657.

$C_{19}H_{18}O_8N_2$ Methyl di-*m*-nitrobenzylmalonate (BAKER and ECCLES), 2127.

$C_{19}H_{19}ON$ 9-Benzoyl-*trans*-hexahydrocarbazole (GURNEY, PERKIN, and PLANT), 2679.

$C_{19}H_{19}O_3N$ 3:11-Dimethoxydihydroprotoberberine, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2271.

$C_{19}H_{19}O_4Cl$ 5-Hydroxy-3:4′-dimethoxy-6:8-dimethylflavylium chloride (ROBERTSON and ROBINSON), 2204.

$C_{19}H_{19}O_5Cl$ 6-Hydroxy-5:7:4′-trimethoxy-4-methylflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3034.
5:6:7:4′-Tetramethoxyflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3037.

$C_{19}H_{19}O_6N$ 2-Carbomethoxyveratrylidenepiperonylmethylamine (MALAN and ROBINSON), 2655.

$C_{19}H_{21}O_2N$ 3:11-Dimethoxytetrahydroprotoberberine, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2271.

$C_{19}H_{21}O_3N_3$ 3-Methoxy-4-benzyloxystyryl methyl ketone semicarbazone (DICKINSON, HEILBRON, and IRVING), 1896.

$C_{19}H_{21}O_3N_5$ Di-*p*-tolylformazylcarboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{19}H_{22}O_2N_2$ Glutarotoluidides (BARNICOAT), 2928.

$C_{19}H_{22}O_6N_2$ Veratrylidenemethoxychromanone oxamino-oxime (PERKIN, RÂY, and ROBINSON), 2097.

19 IV

$C_{19}H_8O_2NCl_7$ Heptachloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2859.

$C_{19}H_9ONCl_6$ *N*-2:4:6-Trichlorophenylbenzimino-2:4:6-trichlorophenyl ether (CHAPMAN), 1747.

$C_{19}H_9O_2NCl_6$ Hexachloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.

$C_{19}H_{10}O_2NCl_5$ 2:6:2′:4′:6′-Pentachloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{10}O_2NBr_5$ Pentabromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2861.

$C_{19}H_{11}O_2NCl_4$ 2:6:2′:4-Tetrachloro-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{12}ONCl_3$ Benzoyl-2:4:6-trichlorodiphenylamine (CHAPMAN), 1748.
N-2:4:6-Trichlorophenylbenziminophenyl ether (CHAPMAN), 1747.

$C_{19}H_{12}O_2NCl_3$ 2:2′:4′-Trichloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{13}ONCl_2$ Benzoyl-2:4-dichlorodiphenylamine (CHAPMAN), 1748.
3:5-Dichloro-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 92.
N-2:4-Dichlorophenylbenziminophenyl ether (CHAPMAN), 1747.

$C_{19}H_{13}ONBr_2$ 3:5-Dibromo-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 95.

$C_{19}H_{13}O_4N_2Br$ *αγ*-Diphthalimido*iso*propyl bromide (MANN), 2912.

$C_{19}H_{14}ONCl$ 5-Chloro-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 93.
Chlorobenzoyldiphenylamines (CHAPMAN), 1748.
Chlorophenylbenziminophenyl ethers (CHAPMAN), 1746.

$C_{19}H_{14}ONBr$ 5-Bromo-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 94.

$C_{19}H_{14}O_2NCl$ 4′-Chloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2856.

$C_{19}H_{14}O_2NBr$ 4′-Bromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.

$C_{19}H_{16}OIAs$ 10-Phenyl-10-methylphenoxarsonium iodide (AESCHLIMANN), 415.

$C_{19}H_{16}O_5NBr$ 6′-Bromo-5:6-dimethoxy-3′:4′-methylenedioxy-1-benzoyl-3:4-dihydro*iso*quinoline (HAWORTH), 2284.

$C_{19}H_{17}O_2N_2I$ 2:2′-Dimethyloxacarbocyanine iodide (HAMER), 2803.

$C_{19}H_{17}NIAs$ 10-Phenyl-10-methyl-5:10-dihydrophenarsazonium iodide (AESCHLIMANN), 416.

$C_{19}H_{17}N_2IS_2$ 2:2′-Dimethylthiocarbocyanine iodide (HAMER), 2802.

$C_{19}H_{18}ONBr$ 6-Bromo-9-benzoylhexahydrocarbazole (GURNEY and PLANT), 1322.

$C_{19}H_{18}O_2NCl$ 3:11-Dimethoxyprotoberberinium chloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2272.

$C_{19}H_{18}O_2NI$ 3:11-Dimethoxyprotoberberinium iodide (CHAKRAVARTI, HAWORTH, and PERKIN), 2272.

$C_{19}H_{18}O_4NBr$ 6′-Bromo-5:6-dimethoxy-3′:4′-methylenedioxy-1 benzyl-3:4-dihydro-*iso*quinoline (HAWORTH), 2284.

$C_{19}H_{20}O_2N_2Br_2$ Pimelo-*p*-bromoanilide (BARNICOAT), 2928.

$C_{19}H_{20}O_4N_2S$ *s*-Dicarbethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 442.

$C_{19}H_{20}O_5BrN$ 6′-Bromo-3′:4′-methylenedioxyphenylaceto-β-2:3-dimethoxyphenylethylamide (HAWORTH), 2284.

19 V

$C_{19}H_9O_2NCl_3Br_4$ Trichlorotetrabromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2864.

$C_{19}H_{10}ONCl_2Br_2$ Trichlorodibromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{10}O_2NCl_2Br_3$ Dichlorotribromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{10}O_3NCl_7S$ Heptachlorobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2859.

$C_{19}H_{11}O_2NCl_3Br$ Trichlorobromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2863.

$C_{19}H_{11}O_2NCl_6S$ Hexachloro-4-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.

$C_{19}H_{12}O_2NBr_5S$ Pentabromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.

$C_{19}H_{13}O_2NCl_5S$ 2:6:2′:4′:6′-Pentachloro-4-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{13}O_3NCl_4S$ 2:6:2′:4′-Tetrachloro-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{14}O_3NCl_3S$ 2:2′:4′-Trichloro-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{14}O_3NBr_3S$ Tribromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.

$C_{19}H_{16}O_2NBrS$ 4′-Bromo-4-*p*-toluenesulphonamidodiphenyl (BELL and ROBINSON), 1131.

19 VI

$C_{19}H_{12}O_3NCl_2Br_3S$ Dichlorotribromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{12}O_3NCl_3Br_2S$ Trichlorodibromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{13}O_3NCl_3BrS$ Trichlorobromosulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2863.

C_{20} Group.

$C_{20}H_{16}O_4$ Benzanthrapurpurin trimethyl ether (CROSS and PERKIN), 1302.

$C_{20}H_{18}O$ Benzhydryl *p*-tolyl ether (HEILBRON and HILL), 2011.

$C_{20}H_{26}S$ Di-α-phenylbutyl sulphide (EVANS, MABBOTT, and TURNER), 1167.

$C_{20}H_{32}O_{14}$ Tetracarbethoxy γ-ethylfructoside (ALLPRESS, HAWORTH, and INKSTER), 1236.

$C_{20}H_{38}O_{13}$ 2:3:4:5-Tetramethylgluconic acid (HAWORTH, LOACH, and LONG), 3154.

$C_{20}H_{40}O_2$ Acid, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1900.

20 III

$C_{20}H_{10}O_8N_6$ 2:3-Di(3′:5′-dinitrophenyl)quinoxaline (CHATTAWAY and COULSON), 579.

$C_{20}H_{12}O_4N_4$ 2:3-Di(3′-nitrophenyl)quinoxaline (CHATTAWAY and COULSON), 578.

$C_{20}H_{12}O_9N_6$ 3:5:3′:5′-Tetranitrobenzil phenylhydrazone (CHATTAWAY and COULSON), 579.

$C_{20}H_{13}O_2N$ 4-Phthalimidodiphenyl (SCARBOROUGH and WATERS), 1140.

$C_{20}H_{14}O_5N_4$ 3:3′-Dinitrobenzil phenylhydrazone (CHATTAWAY and COULSON), 578.

$C_{20}H_{16}O_3N_2$ 2-Acetyl-3-β-phthalimidoethylindole (MANSKE, PERKIN, and ROBINSON), 11.

$C_{20}H_{16}O_4N_2$ αγ-Diphthalimido-β-methylpropane (MANN), 2915.

$C_{20}H_{17}O_2N$ *N*-Phenylbenziminoanisyl ethers (CHAPMAN), 1745.

Benzoylmethoxydiphenylamines (CHAPMAN), 1748.

$C_{20}H_{17}O_2N_3$ Benzenylmethyl-*p*-nitrophenylamidophenylimidine, and its salts (CHEW and PYMAN), 2321.

$C_{20}H_{17}O_2Cl$ 3-*o*-Hydroxyphenyl-5-chlorostyryl-Δ^5-*cyclo*hexen-1-ones (HEILBRON and HILL), 922.

$C_{20}H_{19}O_2N$ Anhydromethyl-3:11-dimethoxytetrahydroprotoberberine, and its hydrochloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2274.

$C_{20}H_{19}O_3N_3$ ζ-Phthalimidohexane-βγ-dione γ-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 9.

$C_{20}H_{20}O_3N_4$ *n*-Butyl 1-phenyl-4:5-diketopyrazoline-3-carboxylate 4-phenylhydrazone (CHATTAWAY and HUMPHREY), 2139.

Ethyl 4:5-diketo-1-tolylpyrazolinecarboxylate tolylhydrazones (CHATTAWAY and HUMPHREY), 2796.

$C_{20}H_{20}O_4N_2$ *N*-Methyl-*N*-β-piperonylethyl-6-aminomethylhomopiperonylonitrile (STEVENS), 132.

$C_{20}H_{20}O_7N_2$ Ethyl bis-*p*-nitrobenzylacetoacetate (BURGESS), 2019.

$C_{20}H_{21}O_4N_3$ ζ-*o*-Carboxybenzamidohexane-βγ-dione γ-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 8.

$C_{20}H_{21}O_5Cl$ 5:6:7:4′-Tetramethoxy-4-methylflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3035.

$C_{20}H_{21}O_6N$ *N*-Methyl-*N*-β-piperonylethyl-6-aminomethylhomopiperonylic acid (STEVENS), 187.

$C_{20}H_{22}O_5N_2$ *N*-Methyl-*N*-β-piperonylethyl-6-aminomethylhomopiperonylamide (STEVENS), 183.

$C_{20}H_{24}O_2N_2$ Adipotoluidides (BARNICOAT), 2928.

$C_{20}H_{26}O_2S$ γγ′-Dibenzyloxydipropyl sulphide (BENNETT and HOCK), 480.

$C_{20}H_{26}O_3S$ Menthyl naphthalenesulphonates, rotation and decomposition of (PATTERSON and MCALPINE), 353.

$C_{20}H_{26}NI$ 4-Phenyl-1-benzyl-1-ethylpiperidinium iodides (MILLS, PARKIN, and WARD), 2621.

20 IV

$C_{20}H_{15}O_2N_2Bi$ Triphenylbismuthine dicyanate (CHALLENGER and WILSON), 211.

$C_{20}H_{15}O_2N_2Sb$ Triphenylstibine dicyanate (CHALLENGER and WILSON), 211.

$C_{20}H_{16}O_3N_4Br_4$ *n*-Butyl dibromophenyl-4:5-diketopyrazoline-3-carboxylate dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{20}H_{16}O_8N_2Be$ Beryllium nitrobenzoylacetones (BURGESS), 2018.

$C_{20}H_{18}O_4N_2S$ 3-Nitro-4-*p*-toluenesulphonmethylamidodiphenyl (BELL and ROBINSON), 1129.

$C_{20}H_{18}O_4N_4Br_4$ Ethyl diketosuccinate 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1326.

$C_{20}H_{19}O_4N_2Br$ *N*-Methyl-*N*-6′-bromo-β-piperonylethyl-6-aminomethylhomopiperonylonitrile, and its salts (STEVENS), 185.

$C_{20}H_{20}O_4N_2Cl$ ζ-*o*-Carboxybenzamidohexane-βγ-dione γ-*m*-chlorophenylhydrazone (MANSKE, PERKIN, and ROBINSON), 10.

$C_{20}H_{22}O_2N_2Br_2$ Subero-*p*-bromoanilide (BARNICOAT), 2928.

$C_{20}H_{23}O_5Cl_4Fe$ 5-Hydroxy-3:3′:4′-trimethoxy-6:8-dimethylflavylium ferrichloride (ROBERTSON and ROBINSON), 2204.

$C_{20}H_{24}O_2NCl$ 3:11-Dimethoxytetrahydroprotoberberine methochlorides (CHAKRAVARTI, HAWORTH, and PERKIN), 2274.

$C_{20}H_{24}O_2NI$ 3:11-Dimethoxytetrahydroprotoberberine methiodides (CHAKRAVARTI, HAWORTH, and PERKIN), 2273.

20 V

$C_{20}H_{12}O_6N_2S_2Na_2$ Sodium 4-sulpho-α-naphthaleneazo-β-naphthyl sulphite (KING), 2644.

$C_{20}H_{20}O_4N_4Br_6S_2$ 1-Amino-5-carbethoxybenzthiazole tribromide (DYSON, HUNTER, and MORRIS), 1190.

C_{21} Group.

$C_{21}H_{12}O_5$ Benzoylalizarin (GREEN), 2931.

$C_{21}H_{14}O_2$ Benzo-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 1702.

$C_{21}H_{14}O_5$ 2:5-Dihydroxybenzaldehyde dibenzoate (HODGSON and BEARD), 2840.

$C_{21}H_{14}O_6$ Diacetyl*iso*benzanthragallol (CROSS and PERKIN), 1302.
Diacetyl*iso*benzflavopurpurin (CROSS and PERKIN), 1305.

$C_{21}H_{14}Cl_2$ 1:5-Dichloro-9-phenyl-10-methylene-9:10-dihydroanthracene (BARNETT, COOK, and WILTSHIRE), 1731.

$C_{21}H_{16}O_2$ 4-Hydroxy-2:2-diphenyl-Δ^3-chromen (HEILBRON and HILL), 2010.

$C_{21}H_{16}N_2$ Amino-2:4-diphenylquinolines (FAWCETT and ROBINSON), 2258.

$C_{21}H_{18}O_2$ 2-Benzoyldi-*p*-tolyl ether (REILLY and DRUMM), 2818.

$C_{21}H_{20}O_8$ Acetylquercetin tetramethyl ether (ATTREE and PERKIN), 239.

$C_{21}H_{20}O_{10}$ *iso*Quercitrin (ATTREE and PERKIN), 237.
$C_{21}H_{20}O_{12}$ Quercimeritrin (ATTREE and PERKIN), 237.
$C_{21}H_{24}O_{12}$ 4-*O*-Tetra-acetylglucosidoxy-2-hydroxybenzaldehyde (ROBERTSON and ROBINSON), 245.
$C_{21}H_{32}O_{11}$ Ethyl $\alpha\beta\beta'$-tricarbethoxy*iso*butyrylsuccinate (ROBINSON and ZAKI), 2413.
$C_{21}H_{40}O_{12}$ Methyl octamethyl cellobionate (HAWORTH, LONG, and PLANT), 2813.
Methyl octamethyl-lactobionate (HAWORTH and LONG), 547.

21 III

$C_{21}H_{15}OCl$ 2-Styryl-β-naphthapyrylium chloride (DICKINSON and HEILBRON), 18.
$C_{21}H_{15}O_4Cl$ 3-*p*-Hydroxystyryl-β-naphthapyrylium chloride (+ $2H_2O$) (DICKINSON and HEILBRON), 18.
$C_{21}H_{15}O_3Cl$ 2-Chlorostyryl-5-methyl-3:4-coumalo-6-benzopyrans (HEILBRON and HILL), 921.
$C_{21}H_{17}O_2N$ Benzoyl-*p*-acetyldiphenylamine (CHAPMAN), 1748.
N-Phenylbenziminoacetylphenyl ethers (CHAPMAN), 1746.
$C_{21}H_{17}N_2Br_3$ *o*-Bromobenzylidene di-*o*-bromobenzylhydrazine (KENNER and WILSON), 1111.
$C_{21}H_{18}O_3N_4$ $\omega\omega$-Dichloro-5-carboxy-2-hydroxyacetophenone osazone (CHATTAWAY and PRATS), 691.
$C_{21}H_{18}O_4N_2$ 6-Methoxy-2-acetyl-3-β-phthalimidoethylindole (MANSKE, PERKIN, and ROBINSON), 13.
$C_{21}H_{18}N_2Br_2$ Benzylidenedi-*o*-bromobenzylhydrazine (KENNER and WILSON), 1111.
$C_{21}H_{19}O_2N$ 3-Benzoylaminodi-*p*-tolyl ether (REILLY and BARRETT), 1400.
$C_{21}H_{21}O_4N_3$ ζ-Phthalimidohexane-$\beta\gamma$-dione γ-*m*-methoxyphenylhydrazone (MANSKE, PERKIN, and ROBINSON), 12.
$C_{21}H_{21}O_5N$ Oxypalmatine (HAWORTH, KOEPFLI, and PERKIN), 553.
$C_{21}H_{21}O_6Cl$ 3-β-Glucosidoxy-7-hydroxyflavylium chloride (ROBERTSON and ROBINSON), 244.
$C_{21}H_{22}O_2N_2$ Normethylstrychnine (CLEMO, PERKIN, and ROBINSON), 1624.
Strychnine (OXFORD, PERKIN, and ROBINSON), 2380.
$C_{21}H_{22}O_5Br_4$ 3:3':4:4'-Tetramethoxydistyryl ketone tetrabromide (DICKINSON, HEILBRON, and IRVING), 1892.
$C_{21}H_{23}O_3N_3$ ζ-*o*-Carboxybenzamidohexane-$\beta\gamma$-dione β-*m*-methoxyphenylhydrazone (MANSKE, PERKIN, and ROBINSON), 12.
$C_{21}H_{24}ON_2$ *iso*Strychnidine (OXFORD, PERKIN, and ROBINSON), 2404.
$C_{21}H_{24}O_2N_2$ Dihydrostrychnines (OXFORD, PERKIN, and ROBINSON), 2393.
$C_{21}H_{24}O_3N_2$ Strychnidone (CLEMO, PERKIN, and ROBINSON), 1613.
*allo*Strychnidone (CLEMO, PERKIN, and ROBINSON), 1615.
$C_{21}H_{25}ON_3$ Aminostrychnidine (OXFORD, PERKIN, and ROBINSON), 2408.
$C_{21}H_{25}O_2N_3$ Strychnidone oxime (CLEMO, PERKIN, and ROBINSON), 1614.
$C_{21}H_{25}O_4N$ Tetrahydropalmatine (HAWORTH, KOEPFLI, and PERKIN), 553.
$C_{21}H_{25}O_5N$ 3:11-Dimethoxytetrahydroprotoberberine methocarbonate (CHAKRAVARTI, HAWORTH, and PERKIN), 2274.
$C_{21}H_{26}ON_2$ Dihydrostrychnidines (OXFORD, PERKIN, and ROBINSON), 2399.
$C_{21}H_{26}O_2N_2$ Pimelotolnilides (BARNICOAT), 2928.
Tetrahydrostrychnine (CLEMO, PERKIN, and ROBINSON), 1600.
$C_{21}H_{26}O_4N_2$ Anhydromethoxymethylstrychnidonic acid (CLEMO, PERKIN, and ROBINSON), 1616.
Dioxyhydroxydihydrostrychnidine (OXFORD, PERKIN, and ROBINSON), 2407.
$C_{21}H_{28}O_3N_2$ Hexahydrostrychnine (OXFORD, PERKIN, and ROBINSON), 2403.

$C_{21}H_{28}O_5N_2$ Dioxyhydroxyhexahydrostrychnine (Oxford, Perkin, and Robinson), 2407.

Methoxymethylstrychnidonic acid (Clemo, Perkin, and Robinson), 1616.

$C_{21}H_{31}O_4N_5$ 2:4-Dinitro-1:3:5-tripiperidinobenzene (Le Fèvre and Turner), 1119.

$C_{21}H_{35}ON_3$ *iso*Pulegone δ-*d*-bornylsemicarbazone (Goodson), 1998.

21 IV

$C_{21}H_{16}O_{13}N_2S_4$ *s*-Carbamides of naphthylaminedisulphonic acids, sodium salts (Balaban and King), 3086.

$C_{21}H_{16}O_{15}N_2S_4$ *s*-Carbamide of 2:8-aminonaphthol-3:6-disulphonic acid, salts (Balaban and King), 3094.

$C_{21}H_{21}O_2N_2I$ 2:2′-Diethyloxacarbocyanine iodide (Hamer), 2803.

$C_{21}H_{21}N_2IS_2$ 2:2′-Diethylthiocarbocyanine iodide (Hamer), 2802.

$C_{21}H_{24}O_2N_2Br_2$ Azelo-*p*-bromoanilide (Barnicoat), 2928.

$C_{21}H_{25}ON_2I$ Strychnidine hydriodide (Clemo, Perkin, and Robinson), 1600.

$C_{21}H_{29}O_4NS$ Benzenesulphonngaiylamide (McDowall), 738.

C_{22} Group.

$C_{22}H_{16}O_2$ Methylbenzo-β-naphtha*spiro*pyrans (Dickinson and Heilbron), 1702.

$C_{22}H_{16}Cl_2$ 1:5-Dichloro-9-phenyl-10-ethylidene-9:10-dihydroanthracene (Barnett, Cook, and Wiltshire), 1731.

$C_{22}H_{18}O$ 2:2-Diphenylmethyl-Δ^3-chromens (Heilbron and Hill), 2010.

$C_{22}H_{18}O_2$ 4-Methoxy-2:2-diphenyl-Δ^3-chromen (Heilbron and Hill), 2010.

$C_{22}H_{18}O_4$ 2-*o*-Carboxybenzoyldi-*p*-tolyl ether and its silver salt (Reilly and Drumm), 2816.

$C_{22}H_{18}O_8$ Tetra-acetylflavopurpurin-anthranol (Cross and Perkin), 1305.

$C_{22}H_{18}N_2$ 8-Methoxy-2:3-diphenyl-5-methylquinoxaline (Dadswell and Kenner), 583.

$C_{22}H_{20}O_2$ 2:4-Diphenyl-3-methylchroman-2-ol (Heilbron and Hill), 2012.

Ethyl triphenylmethane-*o*-carboxylate (Barnett, Cook, and Nixon), 507.

$C_{22}H_{22}O$ Diphenyl-*o*-tolyl carbinyl ethyl ether (Boyd and Hatt), 906.

$C_{22}H_{22}O_4$ Ethyl ββ′-diphenylmuconate (Farmer and Duffin), 411.

$C_{22}H_{26}O_{11}$ ω-*O*-Tetra-acetyl-β-glucosidoxyacetophenone (Robertson and Robinson), 243.

$C_{22}H_{42}O_2$ *iso*Erucic acid, and its zinc salt (Mirchandani and Simonsen), 371.

22 III

$C_{22}H_{15}O_3Cl$ 3-3′:4′-Methylenedioxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron), 19.

$C_{22}H_{16}N_4S$ Di-β-naphthyliminotetrahydrothiodiazole (Baird, Burns, and Wilson), 2533.

$C_{22}H_{17}O_3Cl$ 3-*p*-Methoxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron), 18.

$C_{22}H_{17}O_3Cl$ 3-3′-Methoxy-4′-hydroxystyryl-β-naphthapyrylium chloride (+ $2H_2O$) (Dickinson and Heilbron), 18.

$C_{22}H_{18}O_8N_4$ Ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate (Fairbourne and Fawson), 49.

$C_{22}H_{18}N_4S_2$ Hydrazinedithiocarbo-β-naphthylamide (Baird, Burns, and Wilson), 2533.

$C_{22}H_{22}O_8Cu$ Copper hydroxymethyleneacetoveratrone (Pratt, Robertson, and Robinson), 1981.

$C_{22}H_{23}O_{10}Cl$ 4′-β-Glucosidoxy-5:7-dihydroxy-3-methoxyflavylium chloride (Robertson and Robinson), 1714.

$C_{22}H_{24}O_{22}N_2$ 4:4:5-Trimethyl-Δ^5-*cyclo*pentene-1:3-dicarbanilides (BHAGVAT and SIMONSEN), 85.

$C_{22}H_{25}O_6N_5$ 2:5:3′-Trinitro-4:4′-dipiperidinodiphenyl (LE FÈVRE, MOIR, and TURNER), 2338.

$C_{22}H_{26}ON_2$ Methyl-ψ-strychnidine, and its salts (CLEMO, PERKIN, and ROBINSON), 1603.

$C_{22}H_{27}O_4N$ Anhydromethyltetrahydropalmatines (HAWORTH, KOEPFLI, and PERKIN), 2264.

$C_{22}H_{27}O_5N$ Cryptopalmatine, and its hydrochloride (HAWORTH, KOEPFLI, and PERKIN), 2264.

$C_{22}H_{27}O_7N$ Methyl N-β-veratrylethyl-3:4-dimethoxyhomophthalamate (HAWORTH, KOEPFLI, and PERKIN), 552.

$C_{22}H_{28}ON_2$ Methyldihydrostrychnidine, and its salts (CLEMO, PERKIN, and ROBINSON), 1621; (OXFORD, PERKIN, and ROBINSON), 2402.

$C_{22}H_{28}O_2N_2$ Subero-*o*-toluidide (BARNICOAT), 2928.

$C_{22}H_{28}O_4N_2$ Akuammine, and its salts (HENRY and SHARP), 1954.

22 IV

$C_{22}H_{16}O_5N_6Cl_4$ ωω-Dichloro-3:5-dinitro-2-ethoxyacetophenone osazone (CHATTAWAY and MORRIS), 2016.

$C_{22}H_{25}O_2N_2Br$ Strychnine methobromide (CLEMO, PERKIN, and ROBINSON), 1599.

$C_{22}H_{25}O_2N_2I$ Normethylstrychnine methiodide (CLEMO, PERKIN, and ROBINSON), 1625.

$C_{22}H_{26}O_2N_2Br_2$ Sebaco-*p*-bromoanilide (BARNICOAT), 2928.

$C_{22}H_{26}O_6N_4S$ 3:3′-Dinitro-4:4′-dipiperidinodiphenylsulphone (LE FÈVRE and TURNER), 1117.

$C_{22}H_{27}ON_2Cl$ Methyl*neo*strychnidinium chloride (CLEMO, PERKIN, and ROBINSON), 1611.

Strychnidine methochloride (CLEMO, PERKIN, and ROBINSON), 1601.

$C_{22}H_{27}ON_2Br$ Strychnidine methobromide (CLEMO, PERKIN, and ROBINSON), 1601.

$C_{22}H_{27}ON_2I$ Methyl*neo*strychnidinium iodide (CLEMO, PERKIN, and ROBINSON), 1611.

$C_{22}H_{27}O_2N_2I$ Dihydrostrychnine methiodides (OXFORD, PERKIN, and ROBINSON), 2395.

$C_{22}H_{27}O_{14}N_{10}Co$ Aquo-2:4-dinitrophenoxobisethylene diamminocobaltic 2:4-dinitrophenoxide (DUFF and BILLS), 2374.

$C_{22}H_{28}O_4NCl$ Tetrahydropalmatine methochlorides (HAWORTH, KOEPFLI, and PERKIN), 2263.

$C_{22}H_{28}O_4NI$ Tetrahydropalmatine methiodides (HAWORTH, KOEPFLI, and PERKIN), 2263.

$C_{22}H_{29}ON_2Cl$ Dihydrostrychnidine methochloride (OXFORD, PERKIN, and ROBINSON), 2401.

Methyl*neo*dihydrostrychnidinium chloride (CLEMO, PERKIN, and ROBINSON), 1623.

$C_{22}H_{29}ON_2I$ Dihydrostrychnidine methiodide (OXFORD, PERKIN, and ROBINSON), 2400.

Methyl*neo*dihydrostrychnidinium iodide (CLEMO, PERKIN, and ROBINSON), 1623.

$C_{22}H_{32}O_{16}N_7Co$ Aquo-*p*-nitrophenoxobisethylenediamminocobaltic *p*-nitrophenoxide (DUFF and BILLS), 2373.

C_{23} Group.

$C_{23}H_{14}O_7$ Triacetylbenzanthrapurpurin (CROSS and PERKIN), 1301.

$C_{23}H_{15}N_3$ 5:6-(2′:3′-Diphenylpyrrolo)(4′:5′)-quinoline, and its salts (FAWCETT and ROBINSON), 2256.

$C_{23}H_{18}O_2$ 1:2-Dibenzoyloxy-3-allylbenzene (PERKIN and TRIKOJUS), 1665.

$C_{23}H_{16}Cl_2$ 1:5-Dichloro-9-phenyl-10-propylanthracenes (BARNETT, COOK, and WILTSHIRE), 1731.

1:5-Dichloro-9-phenyl-10-propylidene-9:10-dihydroanthracene (BARNETT, COOK, and WILTSHIRE), 1731.

$C_{23}H_{20}O$ 2:2-Diphenyldimethyl-Δ^3-chromens (HEILBRON and HILL), 2011.

$C_{23}H_{22}O_2$ Diphenyl-2-hydroxy-β:4-dimethylstyrylcarbinol (HEILBRON and HILL), 2011.

$C_{23}H_{22}O_9$ *O*-Triacetyldihydrocarajurinol (CHAPMAN, PERKIN, and ROBINSON), 3024.

$C_{23}H_{26}O_5$ 3:3′-Dimethoxy-4:4′-diethoxydistyryl ketone (DICKINSON, HEILBRON, and IRVING), 1894.

$C_{23}H_{44}O_2$ Methyl *iso*erucate (MIRCHANDANI and SIMONSEN), 375.

23 III

$C_{23}H_{17}ON$ *N*-Phenylbenziminonaphthyl ethers (CHAPMAN), 1745.

$C_{23}H_{17}ON_3$ 9-Methylcarbazole-3-azo-β-naphthol (BURTON and GIBSON), 2386.

$C_{23}H_{17}O_5Cl$ *O*-Benzoylacacetinidin chloride (+ H_2O) (PRATT, ROBERTSON, and ROBINSON), 1978.

$C_{23}H_{19}O_3Cl$ 3-3′:4′-Dimethoxystyryl-β-naphthapyrylium chloride (DICKINSON and HEILBRON), 19.

$C_{23}H_{20}O_6N_4$ Ethyl dibenzeneazochelidonate (MULLEN and CROWE), 1752.

$C_{23}H_{21}O_4Cl$ Ethyl 3-*o*-hydroxyphenyl-5-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylates (HEILBRON and HILL), 921.

$C_{23}H_{21}N_2I$ 1:1′-Dimethyl-4:4′-carbocyanine iodide (HAMER), 2801.

$C_{23}H_{22}O_7N_2$ Ethyl dibenzeneazoacetonedioxalate (MULLEN and CROWE), 1752.

$C_{23}H_{24}O_3N_2$ *O*-Acetyl*iso*strychnine (OXFORD, PERKIN, and ROBINSON), 2396.

$C_{23}H_{26}O_3N_2$ *O*-Acetyldihydro*iso*strychnine (OXFORD, PERKIN, and ROBINSON), 2398.

$C_{23}H_{26}O_4N_2$ Brucine methohydrogencarbonate (GULLAND, PERKIN, and ROBINSON), 1635.

$C_{23}H_{28}O_3N_2$ Brucidine and its salts (GULLAND, PERKIN, and ROBINSON), 1636.

$C_{23}H_{28}O_4N_4$ 3:3′-Dinitro-4:4′-dipiperidinodiphenylmethane (LE FÈVRE and TURNER), 1120.

$C_{23}H_{29}O_5N_3$ Tetrahydrobrucine nitrosoamine, and its hydrochloride (GULLAND, PERKIN, and ROBINSON), 1639.

$C_{23}H_{30}O_2N_2$ Azelotoluidides (BARNICOAT), 2928.

Methoxymethyldihydrostrychnidine (CLEMO, PERKIN, and ROBINSON), 1602.

n-Nonanedicarboxyanilide (BARNICOAT), 2928.

$C_{23}H_{30}O_3N_2$ Oxymethoxymethyl dihydrostrychnidines (CLEMO, PERKIN, and ROBINSON), 1604.

$C_{23}H_{30}O_3N_4$ Strychnidone disemicarbazone (CLEMO, PERKIN, and ROBINSON), 1614.

$C_{23}H_{30}O_4N_2$ Tetrahydrobrucine, and its salts (GULLAND, PERKIN, and ROBINSON), 1638.

$C_{23}H_{32}O_2N_2$ Methoxymethyltetrahydrostrychnidine, and its salts (CLEMO, PERKIN, and ROBINSON), 1617.

23 IV

$C_{23}H_{21}N_2BrS_2$ 2:2′-Diallylthiocarbocyanine bromide (HAMER), 2802.

$C_{23}H_{25}O_3N_3S$ 4-*p*-Sulphobenzeneazobenzyl-*n*-butylaniline, and its sodium salt (REILLY and DRUMM), 1396.

$C_{23}H_{28}O_2N_2Br_2$ *n*-Nonanedicarboxy-*p*-bromoanilide (BARNICOAT), 2928.

$C_{23}H_{28}O_6N_2S$ Strychnine methosulphate (CLEMO, PERKIN, and ROBINSON), 1599.

$C_{23}H_{29}ON_2I$ Methyl-ψ-strychnidine methiodide (CLEMO, PERKIN, and ROBINSON), 1610.

$C_{23}H_{30}O_5N_2S$ Strychnidine methosulphate (CLEMO, PERKIN, and ROBINSON), 1600.

*iso*Strychnidine methosulphate (OXFORD, PERKIN, and ROBINSON), 2405.

$C_{23}H_{30}O_5N_2S$ Dihydrostrychnine methosulphates (OXFORD, PERKIN, and ROBINSON), 2394.

$C_{23}H_{32}ON_2I_2$ Dihydrostrychnidine dimethiodide (OXFORD, PERKIN, and ROBINSON), 2402.

$C_{23}H_{32}O_5N_2S$ Dihydrostrychnidine methosulphate (OXFORD, PERKIN, and ROBINSON), 2400.

$C_{23}H_{33}O_7N_4AS_2$ *s*-Carbamido-3-amino-4-piperidinophenylarsinic acid, and its magnesium salt (KING), 1054.

C_{24} Group.

$C_{24}H_{16}N_2$ Substance, from oxidation of carbazole (MCLINTOCK and TUCKER), 1221.

$C_{24}H_{18}N_2$ 6-Methoxyphenacylideneflavene (IRVINE and ROBINSON), 2093.

$C_{24}H_{22}O_4$ 2-Hydroxy-5-methoxybenzylidenediacetophenone (IRVINE and ROBINSON), 2088.

4-Methoxy-2:2-dianisyl-Δ^3-chromen (HEILBRON and HILL), 2010.

$C_{24}H_{26}N_5$ 3-*mp*-Dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one (DICKINSON, HEILBRON, and IRVING), 1892.

$C_{24}H_{28}N_2$ 6β-*pp'*-Tetramethyldiaminodiphenylstyrene and its dihydrochloride (RODD and LINCH), 2185.

$C_{24}H_{28}O_6$ 3:4-Dimethoxystyryl methyl ketone, dimeride (DICKINSON, HEILBRON, and IRVING), 1893.

$C_{24}H_{29}N_3$ *pp'*-Tetramethyldiaminodiphenyl-*o*-tolylmethylamine (RODD and LINCH), 2177.

24 III

$C_{24}H_{13}N_2Br_4$ 3:6:3':6'-Tetrabromo-9:9'-dicarbazyl (MCLINTOCK and TUCKER), 1216.

$C_{24}H_{12}N_2I_4$ 3:6:3':6'-Tetraiodo-9:9'-dicarbazyl (MCLINTOCK and TUCKER), 1218.

$C_{24}H_{18}O_{12}N_2$ 4:4'-Bis-*op*-dinitrophenyl-2:2'-dinitrodiphenylamine (LE FÈVRE, MOIR, and TURNER), 2337.

$C_{24}H_{17}O_5N_3$ Dibenzoyl-1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid (CHATTAWAY and HUMPHREY), 2136.

$C_{24}H_{18}ON_2$ 2-Keto-1-methyl-5:6-(2':3'-diphenylpyrrole)(4':5')-1:2-dihydroquinoline (FAWCETT and ROBINSON), 2257.

Ketophenylethyldibenzodihydronaphthyridine (HAWORTH and PINK), 2347.

$C_{24}H_{16}O_2N_2$ 1:8-Naphthaldianilide (DAVIES and LEEPER), 1127.

$C_{24}H_{13}O_4N$ *o*-Nitrobenzylidene-*N*-β-phenylethylhomophthalimide (HAWORTH and PINK), 2347.

$C_{24}H_{18}O_4N_2$ *o*-Nitrobenzylidene-*N*-β-phenylethylhomophthalimide (HAWORTH and PINK), 2347.

$C_{24}H_{20}O_2Si$ Diphenoxydiphenylsilicane (KIPPING), 2731.

$C_{24}H_{20}O_6N_4$ *meso*-1:4-Di-*m*-nitrobenzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

$C_{24}H_{23}ON_3$ Ketophenylethyldibenzohexahydronaphthyridine (HAWORTH and PINK), 2348.

$C_{24}H_{22}O_2N_2$ *meso*-1:4-Dibenzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

$C_{24}H_{23}O_4Cl$ Ethyl 3-*o*-methoxyphenyl-5-*p*-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (HEILBRON and HILL), 923.

$C_{24}H_{24}O_2N_4$ *meso*-1:4-Diphenylcarbamyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 345.

$C_{24}H_{26}ON_2$ Benzoylbenzyl-*n*-butyl-*p*-phenylenediamine (REILLY and DRUMM), 1396.

$C_{24}H_{27}O_{10}Cl$ 7-Glucosidoxy-3:3′:4′-trimethoxyflavylium chloride (+H_2O) (ROBERTSON), 246.

$C_{24}H_{27}O_{11}N$ Penta-acetylindican (ROBERTSON), 1941.

$C_{24}H_{27}O_{12}N$ Methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate (ROBERTSON), 1939.

$C_{24}H_{28}O_2N_2$ *pp*′-Tetramethyldiaminodiphenyl-*p*-anisylcarbinol (RODD and LINCH), 2177.

pp′-Tetramethyldiaminodiphenylbenzylcarbinol (RODD and LINCH), 2184.

pp′-Tetramethyldiaminodiphenyl-*o*-tolylcarbinol (RODD and LINCH), 2177.

$C_{24}H_{30}O_3N_2$ Methyl-ψ-brucidine, and its salts (GULLAND, PERKIN, and ROBINSON), 1651.

$C_{24}H_{30}O_4N_4$ 4:4′-Dibromo-3:3′-dinitro-*s*-diphenylethane (LE FÈVRE and TURNER), 1120.

$C_{24}H_{30}O_5N_2$ Acetylakuammine, and its salts (HENRY and SHARP), 1957.

$C_{24}H_{31}O_5N_5$ Brucidone semicarbazone (GULLAND, PERKIN, and ROBINSON), 1652.

$C_{24}H_{32}O_3N_2$ *n*-Decanedicarboxyanilide (BARNICOAT), 2928.

Ethoxymethyldihydrostrychnidine (CLEMO, PERKIN, and ROBINSON), 1616.

Sebacotoluidides (BARNICOAT), 2928.

$C_{24}H_{32}O_3N_2$ Methyl-ψ-dihydrobrucidine, and its dihydriodide (GULLAND, PERKIN, and ROBINSON), 1661.

$C_{24}H_{32}O_4N_2$ Brucidine methoxyhydroxide (+$2H_2O$) (GULLAND, PERKIN, and ROBINSON), 1641.

$C_{24}H_{34}O_3N_2$ Methoxymethyldihydrostrychnidine methohydroxide (CLEMO, PERKIN, and ROBINSON), 1605.

24 IV

$C_{24}H_{17}O_4N_4Br$ Substance, from benzidine and 4:4′-dibromo-3:3′-dinitrodiphenyl (LE FÈVRE and TURNER), 1121.

$C_{24}H_{17}O_{10}N_3S_2$ Nitrobenzoylaminobenzoylnaphthylamine-3:6-disulphonic acids, and their salts (BALABAN and KING), 3079.

$C_{24}H_{17}O_{11}N_3S_2$ 2-*m*′-Nitrobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, salts (BALABAN and KING), 3093.

$C_{24}H_{17}O_{11}N_3S_2$ 1-*m*′-Nitrobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, sodium salt (BALABAN and KING), 3091.

$C_{24}H_{17}O_{13}N_3S_3$ *m*′-Nitrobenzoyl-*m*-aminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, salts (BALABAN and KING), 3095.

$C_{24}H_{19}O_3Cl_4Fe$ 6-Methoxy-4-phenacylflavylium ferrichloride (IRVINE and ROBINSON), 2093.

$C_{24}H_{19}O_8N_3S_2$ Diaminobenzoyl-2-naphthylamine-5:7-disulphonic acids, and their salts (BALABAN and KING), 3082.

$C_{24}H_{19}O_9N_3S_2$ *m*′-Aminobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acids, sodium salts (BALABAN and KING), 3091.

$C_{24}H_{19}O_{11}N_3S_3$ Diaminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, sodium salts (BALABAN and KING), 3096.

$C_{24}H_{20}N_2ClBr_3$ Tri-*o*-bromobenzylhydrazine hydrochloride (KENNER and WILSON), 1111.

$C_{24}H_{23}O_2N_2I$ Methoxymethyldihydrostrychnidine methiodide (CLEMO, PERKIN, and ROBINSON), 1604.

$C_{24}H_{30}O_2N_2Br_2$ *n*-Decanedicarboxy-*p*-bromoanilide (BARNICOAT), 2928.

$C_{24}H_{31}O_3N_2Cl$ Methyl*neo*brucidinium chloride (+H_2O) (GULLAND, PERKIN, and ROBINSON), 1650.

$C_{24}H_{31}O_3N_2I$ Brucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1638.
Methyl*neo*brucidinium iodide (GULLAND, PERKIN, and ROBINSON), 1649.
$C_{24}H_{33}O_3N_2I$ Methyl*neo*dihydrobrucidinium iodide (GULLAND, PERKIN, and ROBINSON), 1659.
$C_{24}H_{33}O_4N_2I$ Tetrahydrobrucine methiodide (GULLAND, PERKIN, and ROBINSON), 1639.
$C_{24}H_{35}O_2N_2I$ Methoxymethyltetrahydrostrychnidine methiodide (CLEMO, PERKIN, and ROBINSON), 1618.

C_{25} Group.

$C_{25}H_{16}O_2$ Di-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 20.
$C_{25}H_{32}O_{11}$ *O*-Penta-acetyldihydrocarajuretinol (CHAPMAN, PERKIN, and ROBINSON), 3026.
$C_{25}H_{26}O_6$ Triphenylmethyl glucose, methylation of (HAWORTH, HIRST, MILLER, and LEARNER), 2443.

25 III

$C_{25}H_{17}O_2Cl$ 3-(β-2′-Hydroxy-1′-naphthylvinyl)-β-naphthapyrylium chloride (DICKINSON and HEILBRON), 19.
$C_{25}H_{18}O_3N_2$ Ketopiperonylethyldibenzodihydronaphthyridine (HAWORTH and PINK), 2347.
$C_{25}H_{18}O_6N_2$ *o*-Nitrobenzylidene-*N*-β-piperonylethylhomophthalimide (HAWORTH and PINK), 2347.
$C_{25}H_{22}O_3N_2$ Ketopiperonylethyldibenzohexahydronaphthyridine (HAWORTH and PINK), 2348.
$C_{25}H_{25}N_2I$ 1:1′-Diethylcarbocyanine iodides (HAMER), 2800.
$C_{25}H_{29}O_5N_3$ 3-*mp*-Dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one semicarbazone (DICKINSON, HEILBRON, and IRVING), 1893.
$C_{25}H_{33}N_2I$ Hexamethylindocarbocyanine iodide (HAMER), 2804.
$C_{25}H_{32}O_4N_2$ *O*-Diacetylhexahydrostrychnine (OXFORD, PERKIN, and ROBINSON), 2404.
$C_{25}H_{32}O_6N_2$ Brucidine methohydrogencarbonate (+ $2H_2O$) (GULLAND, PERKIN, and ROBINSON), 1641.
$C_{25}H_{32}O_6N_2$ Nitromethoxymethyldihydrobrucidine (GULLAND, PERKIN, and ROBINSON), 1647.
$C_{25}H_{34}O_3N_2$ *n*-Nonanedicarboxytoluidides (BARNICOAT), 2928.
n-Undecanedicarboxyaniline (BARNICOAT), 2928.
$C_{25}H_{34}O_4N_2$ Methoxymethyldihydrobrucidine, and its hydriodide (GULLAND, PERKIN, and ROBINSON), 1642.
$C_{25}H_{34}O_5N_2$ Oxymethoxymethyldihydrobrucidine (GULLAND, PERKIN, and ROBINSON), 1643.
$C_{25}H_{34}O_6N_2$ Dioxymethoxymethyldihydrobrucidine (GULLAND, PERKIN, and ROBINSON), 1643.
$C_{25}H_{36}O_4N_2$ Methoxymethyltetrahydrobrucidine, and its salts (GULLAND, PERKIN, and ROBINSON), 1654.

25 IV

$C_{25}H_{32}O_3N_2Br_2$ *n*-Undecanedicarboxy-*p*-bromoanilide (BARNICOAT), 2928.
$C_{25}H_{33}O_3N_2I$ Methyl-ψ-brucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1651.
$C_{25}H_{36}O_2N_2Cl_2$ Methoxymethyldihydrostrychnidine dimethochloride (CLEMO, PERKIN, and ROBINSON), 1607.
$C_{25}H_{38}O_2N_2I_2$ Methoxymethyldihydrostrychnidine dimethiodide (CLEMO, PERKIN, and ROBINSON), 1606.
$C_{25}H_{34}O_2N_2I_2$ Methoxymethyltetrahydrostrychnidine dimethiodide (CLEMO, PERKIN, and ROBINSON), 1620.

C_{26} Group.

$C_{26}H_{16}Cl_2$ 1:5-Dichloro-9:10-diphenylanthracene (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{26}H_{16}Cl_4$ 1:5:9:10-Tetrachloro-9:10-diphenyl-9:10-dihydroanthracene (BARNETT, COOK, and WILTSHIRE), 1729.

$C_{26}H_{17}Cl$ 1-Chloro-9:10-diphenylanthracene (BARNETT, COOK, and WILTSHIRE), 1728.

$C_{26}H_{20}N_2$ 9:9′-Dimethyl-3:3′-dicarbazyl (MAITLAND and TUCKER), 1390.

$C_{26}H_{24}N_2$ *NN′*-Dimethyldiphenylbenzidine (MAITLAND and TUCKER), 1392.

$C_{26}H_{32}O_6$ 3-Methoxy-4-ethoxystyryl methyl ketone, dimeride (DICKINSON, HEILBRON, and IRVING), 1894.

26 III

$C_{26}H_{18}OCl_2$ 1:5-Dichloro-9:10-diphenyl-9:10-dihydroanthranol (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{26}H_{18}O_2Cl_2$ 1:5-Dichloro-9:10-diphenyl-9:10-dihydroanthraquinol (BARNETT, COOK, and WILTSHIRE), 1728.

$C_{26}H_{20}O_4N_6$ 3:3′-Dinitrobenzil osazone (CHATTAWAY and COULSON), 578.

$C_{26}H_{22}O_2N_2$ 1:8-Naphthalbisdimethylanilide (DAVIES and LEEPER), 1127.

$C_{26}H_{26}OSi_2$ Diphenylmethylsilicyl oxide (KIPPING), 106.

$C_{26}H_{36}O_2N_2$ *n*-Decanedicarboxytoluidides (BARNICOAT), 2928.

26 IV

$C_{26}H_{18}O_4N_2As_2$ 10:10′-Bis-4-carboxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 249.

$C_{26}H_{18}O_6N_6S_2$ Dinitrodibenzaldehyde disulphide di-*p*-nitrophenylhydrazones (HODGSON and BEARD), 2424.

$C_{26}H_{22}O_8N_4S_2$ 3:3′-Dinitro-4:4′-di-*p*-toluenesulphonamidodiphenyl (BELL and ROBINSON), 1130.

$C_{26}H_{37}O_4N_2Cl$ Methoxymethyl dihydrobrucidine methochloride (GULLAND, PERKIN, and ROBINSON), 1645.

$C_{26}H_{37}O_4N_2I$ Methoxymethyldihydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1643.

$C_{26}H_{37}O_6N_2I$ Dioxymethoxymethyldihydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1648.

$C_{26}H_{39}O_4N_2I$ Methoxymethyltetrahydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1655.

$C_{26}H_{40}O_8N_2S$ Methoxymethyldihydrobrucidine methosulphate (GULLAND, PERKIN, and ROBINSON), 1645.

26 VI

$C_{26}H_{56}O_9N_2Cl_2S_2Pt_2$ Tetrachloro(triaminopropane-camphor-β-sulphonate) platinum semihydrate (MANN), 1228.

C_{27} Group.

$C_{27}H_{18}Cl_2$ 1:5-Dichloro-9-phenyl-10-benzylanthracene (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{27}H_{20}O_2$ 3:3′-Dimethyldi-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 1703.

$C_{27}H_{22}N_2$ 2:4-Diphenyl-5:6-(4′:5′:6′:7′-tetrahydroindole)(2′:3′)-quinoline (FAWCETT and ROBINSON), 2259.

$C_{27}H_{29}N_3$ *pp′*-Tetramethyldiaminodiphenyl-α-naphthylmethylamine (RODD and LINCH), 2178.

$C_{27}H_{30}O_7$ Ethyl 3-*mp*-dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (DICKINSON, HEILBRON, and IRVING), 1892.

$C_{27}H_{30}O_{16}$ Rutin (ATTREE and PERKIN), 236.

27 III

$C_{27}H_{18}O_6N_4$ Triphthalimidotrimethylamine (KIPPING and MANN), 529.

$C_{27}H_{20}OCl_2$ 1:5-Dichloro-9-phenyl-10-benzyl-9:10-dihydroanthranol (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{27}H_{22}O_2N_2$ Dioxydiphenyltetrahydroindoloquinoline (FAWCETT and ROBINSON), 2260.

$C_{27}H_{24}ON_2$ Phenyl α-tetrahydrocarbazylamino(6)-styryl ketone (FAWCETT and ROBINSON), 2259.

$C_{27}H_{24}O_3N_{10}$ Triphthalylhydrazidotriaminotrimethylamine (KIPPING and MANN), 529.

$C_{27}H_{35}N_2I$ 1:1′-Diallyl-4:4′-carbocyanine iodide (HAMER), 2802.

$C_{27}H_{27}ON_3$ *p*-Benzyl-*n*-butylaminobenzeneazo-β-naphthol (REILLY and DRUMM), 1396.

$C_{27}H_{32}N_2O$ *pp*′-Tetramethyldiaminodiphenylnaphthylcarbinols (RODD and LINCH), 2178.

$C_{27}H_{33}N_2I$ Tetramethyldiethylindocarbocyanine iodide (HAMER), 2804.

$C_{27}H_{38}O_2N_2$ *n*-Undecanedicarboxytoluidides (BARNICOAT), 2928.

27 IV

$C_{27}H_{39}O_4N_2I$ Ethoxymethyldihydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1649.

$C_{27}H_{40}O_4N_2I_2$ Methoxymethyl dihydrobrucidine dimethiodide (GULLAND, PERKIN, and ROBINSON), 1645.

$C_{27}H_{42}O_4N_2Cl_2$ Methoxymethyltetrahydrobrucidine dimethochloride (GULLAND, PERKIN, and ROBINSON), 1657.

$C_{27}H_{42}O_4N_2I_2$ Methoxymethyltetrahydrobrucidine dimethiodide (GULLAND, PERKIN, and ROBINSON), 1656.

$C_{27}H_{42}O_{10}N_2S_2$ Methoxymethyldihydrostrychnidine dimethosulphate (CLEMO, PERKIN, and ROBINSON), 1605.

$C_{27}H_{44}O_{10}N_2S_2$ Methoxymethyltetrahydrostrychnidine dimethosulphates (CLEMO, PERKIN, and ROBINSON), 1619.

C_{28} Group.

$C_{28}H_{16}O_6$ Dibenzoylalizarin (GREEN), 2931.

$C_{28}H_{20}O_2$ 3:3′-Trimethylenedi-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 1704.

$C_{28}H_{24}N_2$ 9:9′-Diethyl-3:3′-dicarbazyl (MAITLAND and TUCKER), 1890.

$C_{28}H_{26}O_2$ Diphenyldi-*o*-tolylpinacol (BOYD and HATT), 905.

$C_{28}H_{34}O_5$ 3-*m*-Methoxy-*p*-propoxyphenyl-5-*m*-methoxy-*p*-propoxystyryl-Δ^5-*cyclo*hexen-1-one (DICKINSON, HEILBRON, and IRVING), 1895.

28 III

$C_{28}H_{18}O_8N_6$ *p*-Azoxydinitrostilbenes (NISBET), 2085.

$C_{28}H_{20}O_5N_4$ *p*-Azoxy-2-nitrostilbene (NISBET), 2085.

$C_{28}H_{21}O_2Cl$ 4-2′-Hydroxy-1′-naphthylidene-1:2:3:4-tetrahydro-8:9-benzoxanthylium chloride (DICKINSON and HEILBRON), 1704.

$C_{28}H_{22}O_3S_4$ 2-*p*-Methoxyphenyl-1:3-benzdithiole 2-oxide (HURTLEY and SMILES), 586.

$C_{28}H_{22}ON_2$ *p*-Azoxystilbene (NISBET), 2084.

$C_{28}H_{23}O_4Cl$ Ethyl 4-*o*-chlorostyracyl-2-phenyl-1:4-benzopyran-3-carboxylate (HEILBRON and HILL), 923.

$C_{28}H_{24}O_3N_2$ 2-*o*-Carboxybenzoyldi-*p*-tolyl ether phenylhydrazone (REILLY and DRUMM), 2817.

$C_{28}H_{25}O_4N_3$ Dibenzoyl derivative of substance $C_{14}H_{13}ON_3$ (KRISHNAMURTI and DEY), 1351.
$C_{28}H_{28}O_4N_2$ Strychnic benzoic anhydride (OXFORD, PERKIN, and ROBINSON), 2409.
$C_{28}H_{36}O_4N_2$ Psychotrine, hydrogen oxalate of (BRINDLEY and PYMAN), 1074.
$C_{28}H_{47}ON$ *iso*Erucic anilide (MIRCHANDANI and SIMONSEN), 375.

28 IV

$C_{28}H_{24}O_2N_2Se_2$ Di-*o*-benzoylmethylaminodiphenyl diselenide (CLARK), 2807.
$C_{28}H_{33}O_{12}N_3Co$ Nitrophenolnitrophenoxobisethylenediamminocobaltic nitrophenoxides (DUFF and BILLS), 2372.

C_{29} Group.

$C_{29}H_{28}N_2$ 4:4′-Tetramethyldiaminodiphenylmethyleneacenaphthene (RODD and LINCH), 2187.
$C_{29}H_{54}O_{16}$ Hendecamelezitose (LEITCH), 591.

29 III

$C_{29}H_{22}O_2N_4$ Triphthalimidotrimethylamine (KIPPING and MANN), 528.
$C_{29}H_{29}N_2Br$ 6:6′-Dimethyl-1:1′-diallyl-2:2′-carbocyanine bromide (HAMER), 2801.
$C_{29}H_{29}N_2I$ 6:6′-Dimethyl-1:1′-diallyl-2:2′-carbocyanine iodide (HAMER), 2801.
$C_{29}H_{30}ON_2$ 4:4′-Tetramethyldiaminodiphenylacenaphthenylcarbinol (RODD and LINCH), 2187.
$C_{29}H_{36}O_4N_2$ Emetamine, and its salts (BRINDLEY and PYMAN), 1075.
$C_{29}H_{38}O_4N_2$ *O*-Methylpsychotrine, and its picrate (BRINDLEY and PYMAN), 1072.
$C_{29}H_{49}ON$ *iso*Erucic *p*-toluidide (MIRCHANDANI and SIMONSEN), 375.

C_{30} Group.

$C_{30}H_{62}$ *n*-Triacontane, oxidation of (FRANCIS and WOOD), 1897.

30 II

$C_{30}H_{22}O_5$ 4′-Hydroxyflavanhydrone (IRVINE and ROBINSON), 2090.
$C_{30}H_{22}O_7$ Trianhydrobisbenzoylacetaldehydephloroglucinol (PRATT, ROBERTSON, and ROBINSON), 1976.
$C_{30}H_{28}N_2$ 4:4′-Tetramethyldiaminodiphenylmethylenefluorene (RODD and LINCH), 2187.
$C_{30}H_{30}O_2$ Tetra-*o*-tolylpinacol (BOYD and HATT), 908.
$C_{30}H_{60}O$ Ketone, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1901.
$C_{30}H_{60}O_2$ Alcohol, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1901.

30 III

$C_{30}H_{20}O_8N_4$ *p*-Azoxy-2-nitro-3′:4′-methylenedioxystilbene (NISBET), 2085.
$C_{30}H_{22}O_{11}N_6$ *p*-Azoxy-2:6-dinitro-4′-methoxystilbene (NISBET), 2085.
$C_{30}H_{24}O_3N_4$ *p*-Azoxybenzylidene-*p*-aminoacetophenone (NISBET), 2084.
$C_{30}H_{24}O_7N_4$ *p*-Azoxy-2-nitro-4′-methoxystilbene (NISBET), 2085.
$C_{30}H_{30}O_2N_4$ 2:2′-Dibenzamidotetramethylbenzidine (BELL and ROBINSON), 1698.

30 IV

$C_{30}H_{24}O_2N_2S_2$ *oo*′-Dicinnamamidodiphenyl disulphide (MILLS and WHITWORTH), 2747.
$C_{30}H_{34}O_4N_4S_2$ 2:2′-Di-*p*-toluenesulphonylamidotetramethylbenzidine (BELL and ROBINSON), 1698.

30 V

$C_{30}H_{24}O_2N_2Br_2S_2$ *oo*′-Dicinnamamidodibromodiphenyl disulphide (MILLS and WHITWORTH), 2747.

C_{31} Group.

$C_{31}H_{24}O_6$ Ethyl di-*p*-naphtha*spiro*pyran-3:3′-dicarboxylate (DICKINSON and HEILBRON), 1704.

31 III

$C_{31}H_{36}ON_2$ *pp*′-Tetraethyldiaminodiphenyl-β-naphthylcarbinol (RODD and LINCH), 2178.

31 IV

$C_{31}H_{42}O_4N_2I_2$ Emetamine dimethiodide (BRINDLEY and PYMAN), 1076.

C_{32} Group.

$C_{32}H_{23}Cl$ 10-Chloro-9:9:10-triphenyl-9:10-dihydroanthracene (BARNETT, COOK, and NIXON), 511.

$C_{32}H_{26}O_7$ 4′-Hydroxy-8-methoxyflavanhydrone (IRVINE and ROBINSON), 2091.

32 III

$C_{32}H_{25}O_4Sb$ Triphenylstibine dibenzoate (CHALLENGER and WILSON), 212.

$C_{32}H_{30}O_5N_6$ *p*-Azoxy-2-nitro-4′-dimethylaminostilbene (NISBET), 2086.

$C_{32}H_{35}O_4Bi$ Triphenylbismuthine dibenzoate (CHALLENGER and WILSON), 212.

C_{33} Group.

$C_{33}H_{30}O_5$ 3:3′-Dimethoxy-4:4′-dibenzyloxydistyryl ketone (DICKINSON, HEILBRON, and IRVING), 1896.

C_{34} Group.

$C_{34}H_{30}O_8$ 3:4:6:3′:4′:6′-Hexamethoxydianthrone (MACMASTER and PERKIN), 1309.

$C_{34}H_{40}N_4$ Octamethyltetra-aminotetraphenylethylene (RODD and LINCH), 2186.

$C_{34}H_{42}O_{20}$ Xanthorhamnin (ATTREE and PERKIN), 286.

$C_{34}H_{46}O_4$ Dimethyl diphenate (BELL and ROBINSON), 1698.

34 III

$C_{34}H_{42}ON_4$ Octamethyltetra-aminotetraphenylethanol (RODD and LINCH), 2186.

34 IV

$C_{34}H_{24}O_{15}N_4S_4$ Azoxy-derivative of *m*-aminobenzoyl-1-naphthylamine-3:6-disulphonic acid, sodium salt (BALABAN and KING), 3079.

C_{35} Group.

$C_{35}H_{26}O_{15}N_4S_4$ *s*-Carbamide of aminobenzoylnaphthylaminedisulphonic acid, sodium salt (BALABAN and KING), 3089.

$C_{35}H_{26}O_{17}N_4S_4$ *s*-Carbamide of 2-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, salts (BALABAN and KING), 3094.

$C_{35}H_{26}O_{17}N_4S_4$ *s*-Carbamide of 1-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, sodium salt (BALABAN and KING), 3092.

$C_{35}H_{26}O_{21}N_4S_6$ *s*-Carbamide of *m*-aminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, sodium salt (BALABAN and KING), 3097.

C_{36} Group.

$C_{36}H_{32}N_2$ Substance, from oxidation of carbazole (MCLINTOCK and TUCKER), 1221.

C_{37} Group.

$C_{37}H_{30}O_6N_2$ Benzylidenebisbenzoylmandelamides (INGHAM), 696.

37 IV

$C_{37}H_{42}O_2N_6As_2$ *s*-Carbamido-3-*m*-aminobenzamido-4-piperidinophenylarsinic acid, and its salts (KING), 1055.

C_{38} Group.

$C_{38}H_{48}N_4$ *αα*-4:4′-Tetramethyldiaminodiphenyl-*ββ*-4:4′-tetramethyldiaminodiphenylethylene (RODD and LINCH), 2186.

38 III

$C_{38}H_{50}ON_4$ *αα*-4:4′-Tetraethyldiaminodiphenyl-*ββ*-4:4′-tetramethyldiaminodiphenylethan-*α*-ol (RODD and LINCH), 2186.

αα-4:4′-Tetramethyldiaminodiphenyl-*ββ*-4:4′-tetraethyldiaminodiphenylethan-*α*-ol (RODD and LINCH), 2186.

C_{39} Group.

$C_{39}H_{28}$ 9:9-Diphenyl-10:10-diphenylmethylene-9:10-dihydroanthracene (BARNETT, COOK, and NIXON), 511.

C_{40} Group.

$C_{40}H_{34}O_2$ *s-oo′*-Dibenzylbenzpinacol (BARNETT, COOK, and NIXON), 509.

C_{49} Group.

$C_{49}H_{36}O_{17}N_6S_4$ *s*-Carbamide of diaminobenzoyl-2-naphthylamine-6:8-disulphonic acid, salts (BALABAN and KING), 3089.

$C_{49}H_{36}O_{19}N_6S_4$ *s*-Carbamides of *m′*-aminobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acids, salts (BALABAN and KING), 3095.

$C_{49}H_{38}O_{22}N_6S_6$ *s*-Carbamide of diaminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, salts (BALABAN and KING), 3097.

C_{52} Group.

$C_{52}H_{38}$ Tetraphenyltetrahydrodianthranyl (BARNETT, COOK, and NIXON), 510.

C_{60} Group.

$C_{60}H_{50}O_2Si_4$ Diphenoxyoctaphenylsilicotetrane (KIPPING), 2732.

ERRATA.

VOL., 1926.

Page	Line	
1995	17	*for* "WILLIAM" *read* "WINSTON."

VOL., 1927.

531	13*	for "*Part XV*" read "*Part XVII.*"
1205	9	*for* "whom he also recommended as his successor" *read* "who is (as well as W. J. de Haas) one of his successors."
1226	Formula V	Insert "$(SCN)_2$" outside the bracket.
2169	Line 22	*for* "280° 189° 250° 250°." *read* ">280° 189° >250° >250°."
2856	26	*for* "boiling acetic acid" *read* "acetic acid."

* From bottom.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, January 20th, 1927, at 8 p.m. In the absence of the President, the Chair was occupied by Dr. ALEXANDER SCOTT, F.R.S., Vice-President.

Reference was made to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
Joseph J. Acworth	March 4th, 1875.	Jan. 3rd, 1927.
George Christopher	June 18th, 1874.	Aug. 7th, 1926.
Frank Cope	Feb. 16th, 1899.	May 12th, 1926.
William B. Hart	May 7th, 1891.	Dec. 29th, 1926.
Frederick H. Painter	Feb. 18th, 1909.	Dec. 12th, 1926.
Edward H. Rennie	Feb. 6th, 1879.	Jan. 1927.
Thomas A. Reid	Dec. 7th, 1893.	Nov. 15th, 1926.
Frederick J. Stoakley	May 5th, 1921.	Jan. 16th, 1927.

The CHAIRMAN announced that the names of the members of Council who retire at the Annual General Meeting on March 24th, 1927, and who are ineligible for re-election to the same office until after the lapse of one year, are as follows :

Vice-President who has filled the office of President :
Prof. W. H. Perkin.

Vice-Presidents who have not filled the office of President :
Mr. A. J. Greenaway and Prof. J. C. Philip.

Ordinary Members of Council :

(*a*) Town Members :
Dr. O. L. Brady, Dr. A. E. Dunstan, and Prof. T. S. Moore.

(*b*) Country Members :
Prof. D. R. Boyd, Mr. B. Lambert, and Prof. F. L. Pyman.

The following vacant places fall due to be filled at the Annual General Meeting on March 24th, 1927, in accordance with the Bye-Laws :

Vice-Presidents who have filled the office of President	One vacancy.
Vice-Presidents who have not filled the office of President	Two vacancies.

Ordinary Members of Council:

(*a*) Town Members ... ... Three vacancies.
(*b*) Country Members ... ... Three vacancies.

Certificates were read for the first time in favour of:

Cameron Gordon Anderson, B.Sc., 23, Warwick Road, Sparkhill, Birmingham.
Gilbert Edward Archey, M.A., 10, Laurie Avenue, Auckland, N.Z.
Eric Sidney Bacon, B.Sc., A.I.C., 78, South Street, Ponders End, Middlesex.
Sydney Thomas Bowden, B.Sc., A.I.C., University College, Newport Road, Cardiff.
Satyendra Nath Chakravarti, M.Sc., 96, Abingdon Road, Oxford.
Lena Winifred Frost, B.Sc., 4, Sandy Lane, Pendleton, Manchester.
Henry Frank Gillbe, B.Sc., A.I.C., 8, Myddleton Buildings, High Street, Islington.
William Honneyman, B.Sc., F.I.C., Ph.C., 17, Cyprus Park, Belfast.
Peter Jayaweera Jayaratne, B.Sc., Seevali School, Ratnapura, Ceylon.
Sin-iti Kawai, Chemical Institute, Tohoku Imperial University, Sendai, Japan.
Alexander Anderson Kennedy, 86, Babbacombe Road, Bromley.
Alkin Lewis, B.Sc., A.I.C., 74, Sutherland Avenue, W. 9.
Rt. Hon. Sir Alfred Moritz Mond, Bart., M.P., 35, Lowndes Square, S.W. 1.
Masuo Murakami, M.Sc., Tohoku Imperial University, Sendai, Japan.
Roger Saxon Nickalls, 61, Elm Park Gardens, S.W. 10.
Mary Alice Marcia Penrose, B.Sc., 9, Grove Road, East Cliff, Bournemouth.
Eric Charles Pickering, Ph.D., B.Sc., A.I.C., 14, Emperor's Gate, South Kensington, S.W. 7.
Stanley Ernest Pusey, 54, Cranbury Road, Fulham, S.W. 6.
Mysore Guru Srinivasa Rao, Central College, Bangalore, India.
Alfred Leonard Read, B.Sc., 154, Southbury Road, Enfield.
Rodney Thomas Shepherd, B.A., Westminster Training College, Horseferry Road, S.W. 1.
Shintaro Ogawa, Tohoku Imperial University, Sendai, Japan.
Walter Lewis Lee Smith, B.Sc., A.I.C., 9, Newton Road, Faversham.
Robert Spence, B.Sc., 18, Croft Avenue, South Shields.
Frederick Robert Storrie, B.Sc., A.I.C., 1, Carriagehill Drive, Paisley.
Robert Bruce Walker, M.A., Buckingham, Que., Canada.
Francis John Watson, M.A., M.Sc., 28, Bishop's Road, Paddington, W. 2.
Albert Greville White, B.Sc., A.I.C., 45, Caledonia Road, Saltcoats.
Robert Scott Wishart, M.A., D.Sc., Copthorne, Fawley.
Norman Edward Wood, B.Sc., 422, Brockley Road, Crofton Park, S.E. 4.
Lakshmi Narayan Yadava, M.Sc., Bareilly College, Bareilly, India.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of:

Clarence A. Hall, 7951, Winston Road, Chestnut Hill, Phila., Pa., U.S.A.
Isaac Silberman, F.I.C., Bedford Pharmacy, Teoville, Johannesburg, S. Africa.

The following papers were read:

"The glow of arsenic." By H. J. Emeléus.

"On the origin of the spectrum of the glow of phosphorus." By H. J. Emeléus and R. H. Purcell.

" Ring-chain tautomerism. Part XVI. The effect of two adjacent *gem*-dimethyl groups on the ease of formation of the *cyclo*-pentane ring." By I. VOGEL.

ORDINARY SCIENTIFIC MEETING, THURSDAY, FEBRUARY 3rd, 1927, AT 8 P.M.

The following papers will be read :

" The nature of the alternating effect in carbon chains. Part XIV. The directive action of some groups of the form –CR'R''·CO·R· in aromatic substitution." By J. W. BAKER and C. K. INGOLD.

" The nature of the alternating effect in carbon chains. Part XVII. The directive action of the groups $\cdot CH_2 \cdot CH_2 \cdot NO_2$, $\cdot CH{:}CH \cdot NO_2$, and $\cdot C(NO_2){:}CHR$ in aromatic substitution." By J. W. BAKER and I. S. WILSON.

" The Storch equation, a general dilution formula, and the validity of the law of mass action at limiting dilutions." By A. FERGUSON and I. VOGEL.

" The calculation of the equivalent conductivity of aqueous solutions of strong electrolytes at infinite dilution. Part II. Application to data at 0°, 18°, and 25° C." By A. FERGUSON and I. VOGEL.

" The calculation of the equivalent conductivity of aqueous solutions of strong electrolytes at infinite dilution. Part III. The mobilities of the hydrogen and the hydroxyl ions." By A. FERGUSON and I. VOGEL.

LECTURE.

A Memorial Lecture in honour of the late Kamerlingh Onnes will be delivered by Professor Dr. Ernst Cohen, of Utrecht, on Thursday, February 10th, 1927, at 8 p.m., at the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1.

ANNUAL GENERAL MEETING AND ANNIVERSARY DINNER.

The Annual General Meeting will be held at Burlington House on Thursday, March 24th, 1927, at 4 p.m., and the Anniversary Dinner will take place the same evening at the Hotel Victoria, Northumberland Avenue, W.C. 2. Further particulars will be circulated later.

List of Papers, or Abstracts thereof, received between December 16th, 1926, and January 20th, 1927. (This List does not include the titles of papers, or abstracts thereof, which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"Acid soaps: a crystalline potassium hydrogen dioleate." By J. W. McBain and A. Stewart.

"Studies of aromatic thionyl and chlorothionyl derivatives. Part I. Thionylcatechol and dichlorothionylquinol." By A. Green.

"The platini-platino chloride electrode. A new type of chlorine electrode." By V. F. Miller and H. Terrey.

"The nature of the alternating effect in carbon chains. Part XIV. The directive action of some groups of the form –CR'R''·CO·R· in aromatic substitution." By J. W. Baker and C. K. Ingold.

"The nature of the alternating effect in carbon chains. Part XV. The directive action of some groups of the form –CO·R in aromatic substitution." By K. E. Cooper and C. K. Ingold.

"The condensation of substituted anilines with *cyclo*pentanone cyanohydrin. Derivatives of 1-anilino*cyclo*pentane-1-carboxylic acid." By S. H. Oakeshott and S. G. P. Plant.

"Synthesis of 5 : 6-dimethoxyindole and its 2-carboxylic acid." By A. E. Oxford and H. S. Raper.

"The condensation of *p*-hydroxybenzoic acid with chloral." By F. D. Chattaway and F. C. y Prats.

"The decomposition products of menthyl esters of sulphonic acids." By T. S. Patterson and I. M. McAlpine.

"The influence of solvents on the rotation of optically active compounds. Part XXIV. Menthyl benzenesulphonate, menthyl naphthalene-α-sulphonate, and menthyl naphthalene-β-sulphonate in various solvents." By T. S. Patterson and I. M. McAlpine.

"The complex chlorides of tervalent molybdenum." By W. R. Bucknall, S. R. Carter, and W. Wardlaw.

"The viscosity of ether at low temperatures." By E. H. Archibald and W. Ure.

"The nitration of benzil, 3 : 5 : 3' : 5'-tetranitrobenzil." By F. D. Chattaway and E. A. Coulson.

"The influence of nitro-groups on the reactivity of substituents in the benzene nucleus. Part IX. 2 : 3- and 2 : 5-Dinitro-4-methoxytoluenes." By H. E. Dadswell and J. Kenner.

"The union of benzoylacetonitrile with organic bases in the presence of salicylaldehyde. Part I." By P. Krishnamurti.

"Aminobenzthiazoles. Part VIII. The effect of substituents on tautomeric systems of the aminothiazole type and the

synthesis of nuclear substituted 1-aminobenzthiazole derivatives." By G. M. DYSON, R. F. HUNTER, and R. W. MORRIS.

"The synthesis of meso-alkyl and meso-aryl anthracene derivatives. Part I." By E. DE B. BARNETT, J. W. COOK, and I. G. NIXON.

"Aminobenzthiazoles. Part IX. The unsaturation of aminothiazoles containing a static triad system, the mechanism of the transformation of arylthiocarbamides into aminobenzthiazole bromides, and the synthesis of some 1-dimethylaminobenzthiazoles." By R. F. HUNTER and E. R. STYLES.

"The velocity of formation of quaternary ammonium salts from trimethylamine and benzyl chloride and the three mononitrobenzyl chlorides." By H. MCCOMBIE, H. A. SCARBOROUGH, and F. F. P. SMITH.

"The nitration of *m*-iodophenol." By H. H. HODGSON and F. H. MOORE.

"The partition of hydrogen chloride between water and benzene." By R. W. KNIGHT and C. N. HINSHELWOOD.

"Pseudo-ternary systems containing sulphur. Part II. The system sulphur–benzoic acid." By D. L. HAMMICK and W. E. HOLT.

"Colour and molecular geometry. Part VI. Explanation of the colours of the anthocyans." By J. MOIR.

"Acid and salt effects in catalysed reactions. Part VI. The embryonic stage of an auto-catalysed reaction. Generalised form of the simple autocatalytic catenary." By H. M. DAWSON.

"The reaction between diazonium salts and malonyldiurethane." By M. A. WHITELEY and D. YAPP.

"The mechanism of the reaction between aluminium–iodine–ethyl alcohol and water. The preparation of ethyl iodide." By A. O. JONES and G. M. GREEN.

"The optical resolution of chloroiodoacetic acid." By A. M. MCMATH and J. READ.

"The preparation of *N*-substituted *o*-benzoicsulphinides." By E. W. MCCLELLAND.

"The nature of the alternating effect in carbon chains. Part XVI. The nitration of some γ-phenylpropylamine derivatives." By C. K. INGOLD and I. S. WILSON.

"On the alleged retardation of certain reactions by light." By A. J. ALLMAND and R. E. W. MADDISON.

"The nature of the alternating effect in carbon chains. Part XVII. The directive action of the groups $\cdot CH_2 \cdot CH_2 \cdot NO_2$, $\cdot CH{:}CH \cdot NO_2$, and $\cdot C(NO_2){:}CHR$ in aromatic substitution." By J. W. BAKER and I. S. WILSON.

" The production of fog in the neutralisation of alkali with hydrogen halides." By H. O. ASKEW.

" The Storch equation, a general dilution formula, and the validity of the law of mass action at limiting dilutions." By A. FERGUSON and I. VOGEL.

" The calculation of the equivalent conductivity of aqueous solutions of strong electrolytes at infinite dilution. Part II. Application to data at 0°, 18°, and 25° C." By A. FERGUSON and I. VOGEL.

" The calculation of the equivalent conductivity of aqueous solutions of strong electrolytes at infinite dilution. Part III. The mobilities of the hydrogen and the hydroxyl ions." By A. FERGUSON and I. VOGEL.

" The mechanism of reactions induced by hydrogen chloride between aromatic aldehydes and aldehydecyanhydrins in solution." By B. H. INGHAM.

" Ring-chain tautomerism. Part XV. The hydroxy-lactone type." By E. ROTHSTEIN and C. W. SHOPPEE.

" Solubility influences. Part IV. The salting-out of aniline from aqueous solutions." By S. GLASSTONE, J. BRIDGMAN, and W. R. P. HODGSON.

" The constitution of the supposed *N*-methylene sulphurous acid derivatives of amines. Part I. Examination by the Elvove method." By G. NEWBERY and M. A. PHILLIPS.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, FEBRUARY 3rd, 1927.

ANDERSON, CAMERON GORDON, 23, Warwick Road, Sparkhill, Birmingham. British. Research Student, Chemistry Dept., University of Birmingham, B.Sc., 1st Class Honours, Chemistry. Priestley Scholar, Chemistry. Frankland Prizeman, Chemistry. (*Signed by*) W. N. Haworth, H. M. Spittle, W. Charlton, H. D. K. Drew, L. W. Needham.

ARCHEY, GILBERT EDWARD, 10, Laurie Avenue, Auckland. British. Secretary, Auckland Institute. M.A. (N.Z.). (*Signed by*) F. P. Worley, W. Frank Short, J. C. Andrews.

BACON, ERIC SIDNEY, 78, South St., Ponders End, Mddx. English. Chemist. B.Sc., 2nd Class Honours Chemistry (London). Associate of the Institute of Chemistry. (*Signed by*) T. J. Drakeley, G. J. Avey, H. J. S. King.

BAGNALL, MARIE, 15, Bent Lane, Heaton Park, nr. Manchester. British. Librarian and abstractor, British Cotton Industry Research Association, Didsbury. B.Sc. (Vict.), 1920. M.Sc. (Vict.), 1925. Thesis: Zymolysis of Starch and Cellulose. (*Signed by*) J. C. Withers, R. G. Fargher, D. Clibbens.

BARR, MOLLIE, Langton, Erith Rd., Belvedere, Kent. British. Student of Chemistry at Bedford College, London University. (*Signed by*) Holland Crompton, J. F. Spencer, Jessie Stewart.

BLOUNT, BERTIE KENNEDY, Idmiston Grange, Idmiston, nr. Salisbury. British. Undergraduate Student of Trinity College, Oxford. Reading for Honours in the School of Chemistry. (*Signed by*) M. P. Applebey, S. G. P. Plant, C. N. Hinshelwood.

BOAKE, EDMOND JOHNSON, Widford Lodge, Chelmsford. British. Director of Companies. Managing Director of A. Boake, Roberts & Co., Ltd., etc., Heavy and Fine Chemical Manufacturers. B.A. Camb. (Honours). (*Signed by*) W. J. Uglow Woolcock, W. H. Perkin, Leonard A. Levy.

BOWDEN, SYDNEY THOMAS, University College, Newport Road, Cardiff. Welsh. Assistant Lecturer and Demonstrator. B.Sc. (Honours), Wales. A.I.C. Formerly Fellow of the University of Wales. (*Signed by*) W. J. Jones, E. P. Perman, N. M. Cullinane.

BUTTERFIELD, GEORGE RICHARD, Selwyn College, Dunedin, N.Z. British. Medical Student. Completed B.Sc. course at Auckland Univ. College. Commencing Medical course at Otago University. I desire to keep in touch with developments of chemistry. (*Signed by*) F. P. Worley, W. F. Short, John R. Hosking.

CHAKRAVARTI, SATYENDRA NATH, 96, Abingdon Road, Oxford. British subject. Research Student in Organic Chemistry, Dyson Perrins Laboratory. B.Sc., First Class. M.Sc. (Organic Chemistry), First Class, of Lucknow University. Studying for D.Phil. at Oxford University. Worked on "The action of toluene sulphonic ester on nitrophenols" under Dr. S. M. Sane, Reader in Organic Chemistry, Lucknow University. (*Signed by*) W. H. Perkin, R. D. Haworth, V. M. Trikojus, S. G. P. Plant.

CHILVERS, CECIL, 29, St. Luke's Avenue, Ilford, Essex. British. Chemist (Anglo-American Oil Company). B.Sc. (London). A.I.C. 1922–1926, Temporary Assistant Chemist, The Government Laboratory. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox, J. F. Hirst.

CLARK, ROBERT EDWARD DAVID, 46, London Road, Southborough, Tunbridge Wells. English. Student. Exhibitioner of St. John's College, Cambridge. Candidate for Natural Science Tripos. (*Signed by*) Hamilton McCombie, Gordon M. Wright, William Blakey.

DAVIES, JOHN STANLEY, 9, Winchester Avenue, Brondesbury, N.W. 6. British. Pharmaceutical Chemist. Bachelor of Science (London, 1925). (*Signed by*) R. H. Doughty, E. H. Williams, R. J. Evans.

DESAI, BHIMBHAI NICHHABHAI, c/o Miss Dickson, 21, Warrender Park Terrace, Edinburgh. Indian. Research Student (King's Buildings, Chemistry Dept., Edinburgh University, Edinburgh). Research Worker and Lecturer in Chemistry (1924–1926), Wilson College, Bombay. Two papers submitted to Indian Science Congress, one in 1924 and the other in 1925. Two papers, one on "Coagulation of Thorium Hydroxide" and the other on "Viscosity Measurements of Ceric Hydroxide Sol and Gel," are in course of publication in the *Journal of Phys. Chemistry*. (*Signed by*) James Walker, Ernest Bowman Ludlam, John E. Mackenzie.

FROST, LENA WINIFRED, 4, Sandy Lane, Pendleton, Manchester. British. Second Mistress at Pendleton High School for Girls, Manchester. In charge of Chemistry Laboratory and all Chemistry Classes. I desire to receive the Society's publications in order to keep in touch with the progress of chemistry. B.Sc., Birmingham. Also studied at the University of Manchester and Salford Technical College. Over 8 years' experience in the teaching of Matri-

culation and Higher School Certificate Chemistry. (*Signed by*) B. Prentice, Vernon Edge, J. W. McMyn, Harold B. Dixon, Frederick Challenger, John F. Wilkinson.

GILLBE, HENRY FRANK, 8, Myddelton Bldgs., High St., Islington. British. Research Student in Physical Chemistry at University College, London. 1st Class Honours B.Sc. in Chemistry (Univ. of London). A.I.C. Paper accepted for publication in the *J.C.S.* in Nov. 1925, entitled: "The Change in the Absorption Spectra of Aromatic Nitro-compounds in Liquid Ammonia with Time," but withdrawn as work was to be extended. (*Signed by*) W. E. Garner, F. G. Donnan, J. N. Collie.

GUJRAL, KIRPAL SINGH SANTOSH, Chhachhi Street, Rawalpindi (Punjab). Indian. Student. Bachelor of Science. LL.B. (St.). (*Signed by*) N. A. Yajnik, E. T. Dean, M. Gopal Rau.

HONNEYMAN, WILLIAM, 17, Cyprus Park, Belfast. British. Research Chemist. B.Sc. (Lond.). F.I.C. (e). Ph.C. (G.B.). Textile Research Chemist, York Street Flax Spinning Co., Ltd., Belfast. (*Signed by*) Henry Wren, Theophilus Harper, J. Carroll Culbert.

HUGHES, HUBERT IVOR, 89, Penchwintan Road, Bangor, N.W. Welsh. Research Student at University College of North Wales, Bangor. B.Sc., Univ. of Wales (Hons. Chemistry), 1924. Sept. 1925— , Research Student at U.C.N.W. (*Signed by*) Kennedy Orton, H. B. Watson, A. E. Bradfield.

HUSBAND, ALFRED DUDLEY, Dept. of Agriculture, Salisbury, S. Rhodesia. English. Chief Agricultural Chemist, Dept. of Agriculture, Salisbury, S. Rhodesia. A.I.C. *Biochem. Journ.*, 1922, **16**, 3; 1923, **17**, 707. (*Signed by*) W. Thomas, W. Godden, J. E. Humphries.

JAYARATNE, PETER JAYAWEERA, Mirissa, Weligama, Ceylon. Sinhalese (British). Headmaster, Seevali School, Ratnapura (Ceylon). B.Sc. (London). (*Signed by*) Norman Rae, J. P. C. Chandrasena, J. R. Bhatt.

JONES, ARTHUR FREDERICK, 12, Colville Terrace, Colville Street, Nottingham. British. Science Master. Bachelor of Science, University of London, with 2nd Class Honours in Chemistry. 1923–26, Science Master, Anglo-Chinese College, Swatow, China. (*Signed by*) F. S. Kipping, J. B. Firth, E. B. R. Prideaux.

JONES, BRYNMOR, "Hilbre," Fronhenlog Terrace, Bangor, N. Wales. British. Research Student at University College of North Wales, Bangor. B.Sc., First Class Honours, Chemistry. (*Signed by*) A. E. Bradfield, H. B. Watson, F. G. Soper.

JONES, DAVID IDRIS, 118, Gough Road, Edgbaston, Birmingham. British. University Student (Research Chemistry, Birmingham). B.Sc. Honours (Chemistry), Second Class (1926), Birmingham. (*Signed by*) W. N. Haworth, S. Peat, W. Charlton, H. D. K. Drew.

KAWAI, SIN-ITI, Chemical Institute, Faculty of Science, Tohoku Imperial University, Sendai, Japan. Japanese. Assistant to Professor Majima in the Tohoku Imperial University, Sendai, Japan, and a Research Student of the Physical and Chemical Research Institute, Hongo, Tokyo. Graduate of the Tohoku Imperial University, Sendai, Japan. Has been engaged in Research Work under Prof. R. Majima, M.I.A., for the last six years. (1) "Synthesis of the Simplest Homologue of Urushiol" (*Scient. Pap. Phys. Chem. Res. Inst., Tokyo*, 1925, **3**, 263; C. 1926, **1**, 3144). (2) "On a New Reaction between Triacetine and Phenol and an Improved Method for the Preparation of Triacetine" (*Scient. Pap. Phys. Chem. Res. Inst.*, 1925, **3**, 275; C. 1926, **1**, 3143). (3) "On the Preparation of Catechol-*ortho*-carboxylic Acid and the Condensation between Catechol and Glycerol" (*Scient. Pap.*

Phys. Chem. Res. Inst., 1925, **3**, 279; C. 1926, **1**, 3144). (*Signed by*) Riko Majima, Shigeru Komatsu, Hiroshi Nomura.

KENNEDY, ALEXANDER ANDERSON, 86, Babbacombe Rd., Bromley, Kent. British. Technical Director of Soap and Toilet Speciality Factory. Member of the Pharmaceutical Society. (*Signed by*) F. C. Dyche-Teague, W. H. Simmons, Percy C. C. Isherwood.

KEYES, ALFRED WILLIAM, 14, Wilson St., Richmond, Auckland, N.Z. English. Student of Chemistry at Auckland University College. About to be employed in chemical industry and wish to keep in touch with the development of chemical science. (*Signed by*) F. P. Worley, A. H. Bowell, W. F. Short, J. C. Andrews.

LEESE, ERNEST, Portland, Whangarei, New Zealand. British. Analyst and Technical Chemist. 3 Years Walthamstow Technical Institute, England. 4 Years Auckland University College. 16 Years' experience as Analyst. Late Assistant to J. A. Pond, Esq., late Govt. Analyst for Auckland. Last 7 years Chief Chemist to Wilson's (N.Z.) Portland Cement, Ltd., Whangarei, N.Z. R.A.M.C. hospital ship work during War. (*Signed by*) J. A. Pond, K. M. Griffin, Alf. J. Parker.

LEWIS, ALKIN, 74, Sutherland Av., Maida Vale, W. 9. British. Student. Have been engaged in Research at King's College since 1923. B.Sc., London, Honours in Chemistry (2nd Class). A.I.C. (*Signed by*) A. J. Allmand, Samuel Smiles, A. Fairbourne.

LINSTEAD, REGINALD PATRICK, 46, Compton Road, Winchmore Hill, N. 21. British. Research Chemist, Imperial College of Science. Ph.D. (London). D.I.C. Joint Author of 3 papers in the Journal of the Society: Trans., 1922, **121**, 2502; 1925, **127**, 616, 815. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, E. F. Linstead.

LOCKTON, EDWARD HUBERT, 62, Pattison Rd., London, N.W. 2. British. Research Student. B.Sc., 1st Class Hons., 1926. A.R.C.S., 1926. (*Signed by*) G. A. R. Kon, R. W. West, John D. Johnson.

LONG, CHARLES WILLIAM, "Mayesvale," Shrubbery Road, Bromsgrove, Worcs. British. Research Student, Chemistry Department, Birmingham University. 1st Class Honours B.Sc. (Birmingham) in Chemistry, June, 1926. Priestley Scholar. (*Signed by*) W. N. Haworth, W. Charlton, H. D. K. Drew, S. Peat.

MOIR, DANIEL DONALD, 116, Orsett Rd., Grays, Essex. British. Student. B.Sc. (Chem. Special). Organic Research Student at East London College. (*Signed by*) E. E. Turner, R. J. W. Le Fèvre, H. A. Mayes.

MOND, The Rt. Hon. Sir ALFRED MORITZ, Bart., M.P., 35, Lowndes Square, London, S.W. 1. British. Chairman, Imperial Chemical Industries, Ltd. (*Signed by*) H. B. Baker, Jocelyn Thorpe, William J. Pope, T. Slater Price, Charles S. Gibson.

MORRIS, MATTHEW, Sewage Works, Hoscar, nr. Ormskirk. British. Chemist and Manager. Student, 4 years, Blackburn Technical College. Member of The Sewage Disposal Works Managers' Association. I also wish to have the use of your library, and to keep in touch with chemical research. (*Signed by*) Harry G. Leigh, W. H. Duckworth, W. E. Speight.

MURAKAMI, MASUO, Faculty of Science, Tohoku Imperial University, Sendai, Japan. Japanese. Research Student in Organic Chemistry at the Tohoku Imperial University. M.Sc. (Tohoku). Engaged at present in research work in Organic Chemistry at the Tohoku Imperial University. (*Signed by*) Riko Majima, Shigeru Komatsu, Hiroshi Nomura.

NICKALLS, ROGER SAXON, 61, Elm Pk. Gds., S.W. 10. British. Under-

graduate, Oxford. Wishes to receive Society's publications, use Library, etc., etc. (*Signed by*) Allan F. Walden, J. Masson Gulland, B. Lambert, Frederick Soddy, C. N. Hinshelwood.

OGAWA, SHINTARO, Institute of Chemistry, Faculty of Science, Tohoku Imperial University, Sendai, Japan. Japanese. Assistant in the Chemical Institute of the Tohoku Imperial University. I graduated at that University in 1926 with dissertation on "The Application of the Perkin Reaction to Phenolic Aldehydes." Now engaged in research work in Organic Chemistry. (*Signed by*) Riko Majima, Shigeru Komatsu, Hiroshi Nomura.

PENROSE, MARY ALICE MARCIA, Woodbury, 9, Grove Road, East Cliff, Bournemouth. English. Teacher of Chemistry. B.Sc., Lond., Chemistry. I desire to have access to the publications of the Society. (*Signed by*) James C. Philip, M. A. Whiteley, H. C. H. Carpenter.

PICKERING, ERIC CHARLES, 14, Emperor's Gate, S. Kensington, S.W. 7. British. Head of Chemistry Dept., The Borough Polytechnic Institute, London. Ph.D. (Glasgow). B.Sc. (London). A.I.C. 5 Years Lecturer in Chemistry, The Royal Technical College, Glasgow. Wilson and Pickering, "Derivatives of Semioxamazide," *J.C.S.*, 1923, **123**, 394; 1924, **125**, 1152; 1925, **127**, 965. (*Signed by*) H. Lambourne, B. R. Heasman, H. S. Bolton.

PUSEY, STANLEY ERNEST, 54, Cranbury Rd., Fulham, S.W. 6. British. Student. Six years' experience at Wellcome Chemical Research Laboratories. Now taking B.Sc. Honours Chemistry course at University College, London. (*Signed by*) T. A. Henry, H. Paget, W. H. Gray, T. M. Sharp, J. A. Goodson, O. L. Brady.

RAO, MYSORE GURU SRINIVASA, Bangalore. Hindu. Professor of Chemistry. (1) Has been a Lecturer since 1908 (Asst. Prof. 1912 and Prof. 1918) (2) Published a paper *J. Amer. Chem. Soc.* (1919) on "*cyclo*Propanes" (with Dr. E. P. Kohler). (3) Published a paper in 1923, "Perfumery and Essential Oil Records." (4) Published a paper in 1925 (*J.C.S.*) "Substitution in Resorcinol Derivatives." (*Signed by*) J. L. Simonsen, Roland V. Norris, M. O. Forster.

READ, ALFRED LEONARD, 154, Southbury Road, Enfield, Mddx. British. Works' Chemist, Enfield Cable Works, Ltd., Brimsdown, Mddx. University College, Southampton, 1918–1921. B.Sc. (Lond.), Honours Chemistry, 1920. (*Signed by*) D. R. Boyd, A. E. Clarence Smith, Bernard W. Crutchlow.

ROBERTSON, ALEXANDER, Cloffrickford, Auchnagatt, Aberdeenshire. British. Assistant Lecturer, Chemistry Dept., Manchester University. M.A. (Aberdeen University, 1919). B.Sc. (Glasgow University, April, 1922). Ph.D. (Glasgow University, 1924). (1) 1923, **123**, 1713. (2) 1923, **123**, 1849. (3) 1924, **125**, 1992. (4) 1926, July, p. 1713. (5) 1926, Aug., p. 1951. (6) 1926, Oct., p. 2761. (*Signed by*) Arthur Lapworth, H. Raymond Ing, Wilson Baker, R. Robinson.

ROWELL, SYDNEY WILLIAM, Christ Church, Oxford. British. Research Student of Christ Church. B.A. *J.C.S.*, 1925, **127**, 2900; 1926, **128**, 1872; 1926, **128**, 1881. (*Signed by*) W. H. Perkin, N. V. Sidgwick, A. S. Russell.

SAUNDERS, BERNARD CHARLES, Pembroke College, Cambridge. British. Research Student. B.A. (Cantab.). 1st Class Honours, Part I, Natural Sciences Tripos. 1st Class Honours, Part II, Natural Sciences Tripos (Chemistry). (*Signed by*) W. J. Pope, W. H. Mills, Gordon E. Watts.

SCHOFIELD, MAURICE, 64, Oakleigh Rd., Clayton, Bradford. British. Senior Science Master, Worksop College, Notts. Student (Chemistry), Magdalen College, Oxford, 1920–1924 (Demyship). Senior Science Master, Worksop College, Notts., at present. B.A. Hons. (Oxon.). B.Sc. Hons.

(London). One year's research, 1923–24. (*Signed by*) E. Hope, N. V. Sidgwick, S. G. P. Plant.

SCHOFIELD, ROBERT KENWORTHY, M.A., Ph.D. University, Durham. British. University Lecturer in Physics, Durham. (*a*) Previous to present appointment part-time Demonstrator and Research Student in Chemical Laboratories, Cambridge. (*b*) *Publications*: Jointly with Dr. E. K. Rideal: "The Kinetic Theory of Surface Films," Parts I and II, *Proc. Roy. Soc.*, 1925, **A, 109**, 57; 1926, **A, 110**, 167. Alone: "An Experimental Verification of Gibbs' Adsorption Equation by Observing the Adsorption by Mercury of its own Ions from Solution, etc.," *Phil. Mag.*, 1926, (7), **1**, 641. (*Signed by*) Irvine Masson, A. Killen Macbeth, G. H. Christie.

SHAW, FLORENCE RUTH, 64, Westfield Rd., Toller Lane, Bradford. British. Research Student, Organic Chemistry, Leeds University. B.Sc., 1st Class Honours Chemistry, Leeds University (1926). (*Signed by*) C. K. Ingold, P. K. Dutt, J. W. Baker, H. M. Dawson, W. Lowson.

SHEPHERD, RODNEY THOMAS, Westminster Training College, Horseferry Rd., S.W. 1. English. Lecturer in Chemistry. B.A. Hons., First Class, Chemistry, Oxford. Research on "The Electrical Absorption of Gases in Quartz Discharge Tubes" (unpublished). "The Direct Synthesis of Nitrous Oxide," Chapman, Shepherd, and Goodman, Trans., June 1926, p. 1404. (*Signed by*) P. C. Austin, H. J. George, D. L. Chapman.

SMITH, WALTER LEWIS LEE-, 9, Newton Rd., Faversham, Kent. British. Temporary Assistant Chemist, Government Laboratory. B.Sc. (London). A.I.C. (*Signed by*) R. Robertson, A. More, Geo. Stubbs, Ernest M. Hawkins, B. D. Porritt.

SNOW, PERCY HENRY, "Lamorna," Greenhill Road, Moseley, Birmingham. British. Managing Director and Chief Chemist of the Eclipsol Oil Co., Ltd. Desires admission to the Society as Research Chemist in Lubricating Oils; much work being done at the request of other oil firms, and of a secret nature. (*Signed by*) Joseph Lones, Arthur Adams, J. H. Wood.

SPEDDING, KENNETH, Mounthill House, Chickenley Lane, Dewsbury. British. Student in Chemistry. I desire to follow the progress of chemical investigation. (*Signed by*) Irvine Masson, C. W. Gibby, A. Killen Macbeth. G. H. Christie.

SPEIGHT, RONALD, 8, Park View, Thornhill, Dewsbury, Yorks. British Student in Chemistry. I desire to keep in touch with the development of chemistry. (*Signed by*) Irvine Masson, A. Killen Macbeth, G. H. Christie, C. W. Gibby.

SPENCE, ROBERT, 18, Croft Avenue, South Shields. British. Research Student at Armstrong College, Newcastle-on-Tyne. 1st Class Hons. B.Sc. (Chemistry), Univ. of Durham, 1926. Shared Senior Pemberton Scholarship, 1925. Shared Freire-Marreco Prize and Medal, 1926. (*Signed by*) G. R. Clemo, H. V. A. Briscoe, P. L. Robinson.

STARK, ALLAN RAMSAY, 61, St. Vincent Crescent, Glasgow, C. 3. Scottish. Assistant Analyst, Anglo-Persian Oil Co., Ltd., Meadhurst, Sunbury-on-Thames, Middlesex. B.Sc. (Hons.), Glasgow. A.I.C. (*Signed by*) Thomas Gray, F. J. Wilson, R. M. Caven, M. M. J. Sutherland, W. M. Cumming.

STEELE, ALFRED RAYMOND, 24, Newlands Avenue, West Hartlepool. British. Research Student. B.Sc. Lond., 1st Class. Honours, Chemistry. (*Signed by*) F. S. Kipping, B. D. Shaw, F. C. Laxton.

STEVENS, MARY ELIZABETH, 521, King's Rd., Chelsea, S.W. 10. British. Student. Student of Chemistry in the University of London. (*Signed by*) Holland Crompton, J. F. Spencer, Jessie Stewart.

STORRIE, FREDERICK ROBERT, B.Sc. (Glas.), A.I.C., 1, Carriagehill Drive, Paisley. Scots. Assistant to the Gardiner Professor of Organic Chemistry, The University of Glasgow. Part-time Demonstrator in Chemistry to Students of Engineering, 1923–26; Assistant in Org. Chemistry, 1926– ; Research Student, 1923–26 (University of Glasgow). No papers published. (*Signed by*) T. S. Patterson, J. Roberts, S. Horwood Tucker, G. G. Henderson, T. S. Stevens.

STORY, CHARLES WILLIAM HERBERT, Woodside Vicarage, Horsforth. English. Student at Leeds University. 1st Class Honours B.Sc. (Technology). 12 Months' Research. M.Sc. (Technology). (*Signed by*) C. K. Ingold, R. B. Forster, A. G. Perkin.

TAPLEY, RICHARD ARTHUR BEATER, 234, Evering Road, Clapton, E. 5. British. Temporary Assistant Chemist, Government Laboratory. B.A. (2nd Class Hons.), Chemistry, Oxon. B.Sc., Chemistry, Oxon, 1924. Perkin and Tapley, *J.C.S.*, 1924, **125**, 2428. (*Signed by*) R. Robertson, Geo. Stubbs, A. More.

TURNER, ARTHUR, 235, College St., Long Eaton, Nottingham. British. Chemical Research at University College, Nottingham. B.Sc. (Lond.). A.I.C. (*Signed by*) F. S. Kipping, J. B. Firth, B. D. Shaw, F. C. Laxton.

VIRDEN, CYRIL JOSEPH, 24, Richmond Rd., Oxford. British. Research Student at Dyson Perrin Laboratory, Oxford. Passed Part I Final Honours School of Chemistry of the University of Oxford. (*Signed by*) W. H. Perkin, J. M. Gulland, S. G. P. Plant, E. Hope.

WALKER, ROBERT BRUCE, Buckingham, Que., Canada. Canadian–Scotch extraction. Research Assistant in Chemistry for Electric Reduction Co., Ltd. B.A. and M.A., Toronto. Two terms Assistant in Chemistry, Toronto University. Publication: *Trans. Amer. El. Chem. Soc.*, **46**, 205. (*Signed by*) Alfred E. Macintyre, Frank T. Shutt, Frank G. Wait.

WARD, GILBERT OAKLEY, 325, Superior Ave., Cleveland, Ohio, U.S.A. American. Technical Librarian, Cleveland Public Library. Graduate of Columbia College. A.B. P.B.K. Work involves co-operation with chemists and chemical engineers in research into chemical literature; also supervision of such work. Active Member Cleveland Engineering Society. (*Signed by*) Olin F. Tower, H. T. Clarke, Edmund B. Middleton.

WATSON, FRANCIS JOHN, 28, Bishop's Rd., Paddington, W. 2. British. Lecturer in Chemistry, Working Men's College, Melbourne. M.A. M.Sc. (Melb.). (*Signed by*) James C. Philip, A. A. Eldridge, M. S. Shah.

WHITE, ALBERT GREVILLE, B.Sc. (Wales), A.I.C., "Arthurlie," 45, Caledonia Rd., Saltcoats. Welsh. Research Scientist, Nobel Industries, Ltd. Author of various communications on the ignition and propagation of flame in gas- and vapour-air mixtures, including: *J.C.S.*, 1919, **115**, 1248 and 1462; 1922, **121**, 1244, 1688, and 2561; 1924, **125**, 2387; 1925, **127**, 48 and 672. (*Signed by*) Wm. Barbour, W. J. Jenkins, F. D. Miles.

WHITE, EDMUND, 16 and 17, Cross Street, Hatton Garden, London, E.C. 1. British. Chemical Manufacturer. Desires to receive the publications of the Society. (*Signed by*) H. B. Baker, C. S. Gibson, Robert H. Pickard.

WISHART, ROBERT SCOTT, Copthorne, Fawley, Hants. British. Assistant Superintendent, Petroleum Oil Refinery. M.A., D.Sc. (Edinburgh). "Synthesis of Inosit" (with H. Wieland), *Ber.*, June, 1914, p. 2082. Research Chemist, B.D.C. (1919–25). "Constitution of *iso*Cyanine" (with W. H. Mills), *J.C.S.*, 1920. (*Signed by*) W. H. Perkin, F. H. Garner, W. H. Mills.

WOOD, NORMAN EDWARD, 422, Brockley Rd., Crofton Park, S.E. 4. British. Research Student. B.Sc. (1st Class Hons., Chemistry, Bristol). "The

Boiling Points of some *n*-Aliphatic Hydrocarbons " (1926, p. 1420). (*Signed by*) F. Francis, R. C. Menzies, T. Malkin.

YADAVA, LAKSHMI NARAYAN, Bareilly. Indian. Professor of Chemistry, Bareilly College. M.Sc., Allahabad University. Has been teaching chemistry for the last 12 years. Published " Notes on Qualitative Analysis of Single Salts and a Chart for Group Analysis of Inorganic Bases." (*Signed by*) K. C. Pandya, N. A. Yajnik, E. T. Dean.

YAMAMOTO, RYO, Chemical Department, University, Manchester. Japanese. Professor of the Agricultural College of Taiwan, Japan. Graduate of Tohoku University, Japan. Dr. of Agricultural Chemistry of Tokyo University. Have done Research Work under Prof. U. Suzuki, M.I.A., 10 years. Wrote a paper, " On the Insecticidal Principle of Insect Powder " (*Sci. Paper of the Inst. of Ph. and Chem. Res. in Tokyo*, 1925, **3**, 193). Now working under Prof. R. Robinson, F.R.S., in the University, Manchester. (*Signed by*) Robert Robinson, Arthur Lapworth, Ernest W. Wignall.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

HALL, CLARENCE A., 7951, Winston Road, Chestnut Hill, Phila., Pa. American Citizen. Asst. Factory Engineer, Electric Storage Battery Co., Philadelphia, Penn. Graduate of University of Pennsylvania, Class, 1896. Member of following societies: American Institute of Chemical Engineers, American Institute of Mining and Metallurgical Engineers, American Electrochemical Society, American Chemical Society, American Ceramic Society, Faraday Society, Society of Chemical Industry, Franklin Institute (Member Board Managers—Chairman of the Committee of Science and Arts). For 30 years chemical, electro-chemical, and chemical engineering work has occupied my time. U.S. as well as foreign patents cover some of my work. I have neither published nor delivered any papers; corporations as a rule are not eager to make public the investigations, improvements, or changes in their methods. (*Signed by*) Wilder D. Bancroft.

HARRIS, CECIL EDWARD GADWIN, 188, Montpelier Rd., Durban, Natal, S.A. British South African. Chemist and Druggist. Late Student of the Natal Technical College. (*Signed by*) Charles Douglas Golding.

MOITRA, GANESH CHANDRA, 42, Barr Street, Rangoon. Bengalee Hindu. Assistant Chemist, Harcourt Butler Institute of Public Health, Burma, Rangoon. (1) Passed the B.Sc. degree Exam. of the Calcutta University in 1919 with distinction (with Physics, Chemistry, and Maths.). (2) Served for about 2 years as Chief Chemist in the Howrah Flour Mills, Bengal. (3) Working for about 3 years as Lecturer in Physics and Chemistry in the Govt. Training Class for Public Health Inspectors, Rangoon. (*Signed by*) Thein Kin, Maung Ba San.

SILBERMAN, ISAAC, Bedford Pharmacy, Yeoville, Johannesburg, S.A. British. Chemist and Druggist. Late Lecturer Physics, Johannesburg College. Demonstrator Practical Chemistry. F.I.C. Student. (*Signed by*) Bennett A. Jacobson, Max Rubin.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ABDERHALDEN, EMIL. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I. Chemische Methoden, Teil II, Heft ii. Berlin 1926. pp. 71 to 216. ill. (*Recd.* 7/1/27.)

From the Publishers : Herren Urban & Schwarzenberg.

BRYANT AND MAY MUSEUM OF FIRE-MAKING APPLIANCES. Catalogue of the exhibits. Compiled, with an introduction and notes, by MILLER CHRISTY. London 1926. pp. viii + 255. ill. (*Reference.*) 5*s.* net.

From the Publishers : Messrs. Bryant & May, Ltd.

KENT-JONES, DOUGLAS WILLIAM. A study of the effect of heat upon wheat and flour especially in relation to strength. Dover 1926. pp. vi + 116. ill. (*Recd.* 22/12/26.)

From the Author.

KOLTHOFF, J. M. With the collaboration of HEINRICH MENZEL. Die Massanalyse. Teil I. Die theoretischen Grundlagen der Massanalyse. Berlin 1927. pp. xii + 254. ill. *M.* 10.50. (*Recd.* 14/1/27.) From the Publisher : Herr Julius Springer.

RESEARCH ASSOCIATION OF BRITISH FLOUR-MILLERS. 2nd Annual Report, 1924–25, etc. London 1925 +. From the Director.

SANO, SHIZUWO. Scientific papers. Tokyo 1926. pp. xii + 340. (*Recd.* 5/1/27.) From the Publishing Committee.

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. The cleaning and restoration of museum exhibits : third report upon investigations conducted at the British Museum. London 1926. pp. 70 + 58 plates. (*Reference.*) 5*s.* net. From the Director.

THOMS, HERMANN. Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. VI. Part ii. Berlin 1926. pp. 241 to 480. *M.* 10. (*Recd.* 22/12/26.)

From the Publishers : Herren Urban & Schwarzenberg.

THORPE, JOCELYN FIELD, and WHITELEY, MARTHA ANNIE. A student's manual of organic chemical analysis, qualitative and quantitative. Reissue, with appendix on new methods of organic analysis, by HENRI TER MEULEN and J. HESLINGA. London 1926. pp. x + 250. ill. 9*s.* net. (*Recd.* 17/1/27.)

From the Authors.

II. *By Purchase.*

CLAUDE, GEORGES. Air liquide, oxygène, azote, gaz rares. 2nd edition. Paris 1926. pp. iv + 424. ill. 32 *fr.* (*Recd.* 22/12/26.)

CUSHNY, ARTHUR ROBERTSON. Biological relations of optically isomeric substances. London 1926. pp. ix + 80. ill. 9*s.* net. (*Recd.* 17/1/27.)

FRITZ, FELIX. Das Linoleum und seine Fabrikation mit besonderer Berücksichtigung seiner Geschichte, Eigenschaften und Verwendung. Berlin [1926]. pp. 377. ill. *M.* 25. (*Recd.* 29/12/26.)

GATTEFOSSÉ, R. M. Distillation des plantes aromatiques et des parfums. Paris 1926. pp. vi + 152. ill. 16.50 *fr.* (*Recd.* 29/12/26.)

KAYSER, HEINRICH. Tabelle der Hauptlinien der Linienspektra aller Elemente nach Wellenlänge geordnet. Berlin 1926. pp. viii + 198. *M.* 24. (*Recd.* 30/12/26.)

KEGHEL, MAURICE DE. Traité général de la fabrication des colles, des glutinants et matières d'apprêts. Paris 1926. pp. iv + 714. ill. 154 *fr.* (*Recd.* 29/12/26.)

LORENZ, RICHARD, and EITEL, WILHELM. Pyrosole: das kolloide Phänomen in der glühend flüssigen Materie und seine Erstarrungs-zustände. Unter Berücksichtigung des latenten photographischen Bildes. (Kolloidforschung in Einzeldarstellungen.) Leipzig 1926. pp. x + 290. *M.* 20. (*Recd.* 18/12/26.)

MARK, HERMANN. Die Verwendung der Röntgenstrahlen in Chemie und Technik. Leipzig 1926. pp. xvi + 528. ill. *M.* 50. (*Recd.* 29/12/26.)

MEYER, JULIUS. Der Gaskampf und die chemischen Kampstoffe. 2nd edition. Leipzig 1926. pp. xiv + 470. ill. *M.* 20. (*Recd.* 18/12/26.)

MÖHLAU, RICHARD, and BUCHERER, HANS THEODOR. Farbenchemisches Praktikum. 3rd edition. Berlin 1926. pp. x + 390 + 7 pattern cards. *M.* 22. (*Recd.* 18/12/26.)

MÜLLER, ERICH. Die elektrometrische (potentiometrische) Massanalyse. 4th edition. Dresden 1926. pp. viii + 246. ill. *M.* 14. (*Recd.* 18/12/26.)

NERNST, WALTHER. Theoretische Chemie. 11th–15th edition. Stuttgart 1926. pp. xvi + 928. ill. *M.* 50. (*Recd.* 21/12/26.)

RYSCHKEWITSCH, EUGEN. Graphit: Charakteristik, Erzeugung, Verarbeitung und Verwendung. Leipzig 1926. pp. xii + 324. ill. *M.* 16.50. (*Recd.* 18/12/26.)

SCHEIBER, JOHANNES, with the collaboration of KURT SÄNDIG. Lacke und ihre Rohstoffe. Leipzig 1926. pp. xviii + 642. ill. *M.* 32.40. (*Recd.* 29/12/26.)

SCHŒN, M. Le problème des fermentations: les faits et les hypothèses. Paris 1926. pp. iv + 200. ill. 21.50 *fr.* (*Recd.* 22/12/26.)

SÜVERN, KARL. Die künstliche Seide: ihre Herstellung und Verwendung. 5th edition. With the collaboration of H. FREDERKING. Berlin 1926. pp. xx + 1108. ill. *M.* 64.50. (*Recd.* 29/12/26.)

VERNE, J. Les pigments dans l'organisme animal : chimie, morphologie, physiologie, éthologie. Paris 1926. pp. xvi + 604. ill. 28 *fr.* (*Recd.* 29/12/26.)

WEIMARN, PETR PETROVIČ VON. Die Allgemeinheit des Kolloidzustandes : kolloides und kristalloides Lösen und Niederschlagen. Translated from the Russian by S. F. SLOKASOW. 2nd edition. Edited by ALFRED KUHN. Vol. I. Dresden 1925. pp. xvi + 506. ill. *M.* 27. (*Recd.* 18/12/26.)

III. *Pamphlets.*

GUILD, JOHN. A trichromatic colorimeter suitable for standardisation work. (From the *Trans. Optical Soc.*, 1925–6, 27.) ill.

MINES DEPARTMENT. *Safety in Mines Research Board.* Paper No. 29. The pressure wave sent out by an explosive. Part II. By WILLIAM PAYMAN and W. C. F. SHEPHERD. London 1926. pp. 28. ill.

NIELSEN, ROGER. The Emil Christian Hansen Memorial erected in Ribe by the Alumni Association of the Wahl-Henius Institute, Chicago. Copenhagen [1926]. pp. 30.

PENFOLD, ARTHUR RAMON. Some industrial uses of the oil of Eucalyptus phellandra. (*Sydney Technological Museum Bulletin*, No. 11.) 1926. pp. 6.

ROTH, GEORGE B. A consideration of arsphenamine and certain other organic arsenic compounds used in the treatment of syphilis. (From the *U.S. Public Health Reports*, 1921, 36.)

—— Keeping qualities of market samples of neoarsphenamine while in ampule. (From the *U.S. Public Health Reports*, 1921, 36.)

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. Report of test on the "fusion" rotary retort installed at the works of Electrobleach and By-products, Ltd. London 1926. pp. vi + 21. ill.

—— The anodic oxidation of aluminium and its alloys as a protection against corrosion. London 1926. pp. iv + 40. ill.

—— Second Report of the Gas Cylinders Research Committee. (Periodical heat treatment.) London 1926. pp. iv + 29 + 13 plates.

—— *Building Research.* Technical Paper No. 3. The permeability of Portland cement concrete. By W. H. GLANVILLE. London 1926. pp. vi + 50. ill.

—— —— Technical Paper No. 4. The determination of free lime in hydraulic cement. By FRANK LAWRENCE BRADY and FRANCIS JOHN MCCONNELL. London 1926. pp. iv + 13.

—— —— Technical Paper No. 5. The consistence of cement pastes, mortars, and concrete. By N. DAVEY. London 1926. pp. viii + 54. ill.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, February 3rd, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Charles E. Beadnell	Feb. 7th, 1861.	Jan. 26th.
John Webster	May 6th, 1909.	Jan. 20th.

Neilson Brown and R. W. Morris were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of:

David Henry Burton, B.Sc., A.R.C.S., A.I.C., 49, Rayleigh Road, Wimbledon, S.W. 19.
Edwin Herbert Bunce, A.I.C., 37, Northcote Road, Walthamstow, E. 17.
Edgar Dawn Copley, B.A., B.Sc., 36, Lee Terrace, Blackheath, S.E. 3.
John Gurney, B.A., Walsingham Abbey, Norfolk.
Leonard Joseph Hooley, B.A., A.I.C., 11, Newhouse Road, Grangemouth.
George Robert Howard, B.Sc., 32, Gilpin Street, Peterborough.
Arthur William Knapp, B.Sc., F.I.C., Trinidad, Pine Apple Rd., King's Heath, Birmingham.
Herbert Joseph Millward, Ivydene, Gravelly Lane, Erdington, Birmingham.
Otto Leslie Shaw, Betula, Park View Road, New Eltham, S.E. 9.
Allan George Tyler, B.Sc., 48, Bentley Street, Lockwood, Huddersfield.
Albert Denny Usher, B.Sc., 106, Bolingbroke Grove, S.W. 11.

The following papers were read:

"The nature of the alternating effect in carbon chains. Part XIV. The directive action of some groups of the form $-CR'R''\cdot CO\cdot R$ in aromatic substitution." By J. W. BAKER and C. K. INGOLD.

"The nature of the alternating effect in carbon chains. Part XVII. The directive action of the groups $\cdot CH_2\cdot CH_2\cdot NO_2$, $\cdot CH{:}CH\cdot NO_2$, and $\cdot C(NO_2){:}CHR$ in aromatic substitution." By J. W. BAKER and I. S. WILSON.

"The Storch equation, a general dilution formula, and the validity of the law of mass action at limiting dilutions." By A. FERGUSON and I. VOGEL.

"The calculation of the equivalent conductivity of aqueous solutions of strong electrolytes at infinite dilution. Part II. Application to data at 0°, 18°, and 25° C." By A. FERGUSON and I. VOGEL.

"The calculation of the equivalent conductivity of aqueous solutions of strong electrolytes at infinite dilution. Part III. The mobilities of the hydrogen and the hydroxyl ions." By A. FERGUSON and I. VOGEL.

Meeting held in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, S.W. 1, on Thursday, February 10th, 1927, at 8 p.m., Professor H. BREREton BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

Professor Dr. Ernst Cohen delivered the Kamerlingh-Onnes Memorial Lecture. A vote of thanks to the Lecturer, proposed by Professor F. G. Donnan, F.R.S., and seconded by Sir James Walker, F.R.S., was carried with acclamation, Professor Dr. Cohen making acknowledgment.

Ordinary Scientific Meeting, Thursday, February 17th, 1927, at 8 p.m., Professor H. BREREton BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of:

Charles McKenley Cameron, 146, Whalley Road, Clayton-le-Moors, Accrington.
Richard Chadwick, B.A., 101, Whitefriar's Avenue, Wealdstone.
Ronald Kington Christy, B.Sc., 3, Crieff Road, Wandsworth, S.W. 18.
William Herbert Hatfield, D.Met., Muswell Lodge, Brincliffe Crescent, Sheffield.
James Hutchison McGregor, A.I.C., Avenue Cottage, Alexandria, Dumbartonshire.
Tarak Nath Majumdar, 11, Belvedere Road, Calcutta, India.
Dorothy May Lyddon Rippon, B.A., Springfield House, Abingdon, Berks.
Carl Rowen Ward, B.A., Woodcroft, Newburn, Northumberland.
Charles Barnett Wingfield, 36, Clarendon Gardens, Wembley.

Dr. A. D. Mitchell and Mr. H. Paget were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Cameron Gordon Anderson, B.Sc.
Gilbert Edward Archey, M.A.
Eric Sidney Bacon, B.Sc., A.I.C.
Marie Bagnall, M.Sc.
Mollie Barr.
Bertie Kennedy Blount.
Edmond Johnson Boake, B.A.
Sydney Thomas Bowden, B.Sc., A.I.C.
George Richard Butterfield.
Satyendra Nath Chakravarti, M.Sc.
Cecil Chilvers, B.Sc., A.I.C.
Robert Edward David Clark.
John Stanley Davies, B.Sc.
Bhimbhai Nichhabhai Desai.
Lena Winifred Frost, B.Sc.
Henry Frank Gillbe, B.Sc., A.I.C.
Kirpal Singh Santosh Gujral, B.Sc., LL.B.
Clarence A. Hall.

Cecil Edward Gadwin Harris.
William Honneyman, B.Sc., F.I.C.
Hubert Ivor Hughes, B.Sc.
Alfred Dudley Husband, A.I.C.
Peter Jayaweera Jayaratne, B.Sc.
Arthur Frederick Jones, B.Sc.
Brynmor Jones, B.Sc.
David Idris Jones, B.Sc.
Sin-Iti Kawai.
Alexander Anderson Kennedy.
Alfred William Keyes.
Ernest Leese.
Alkin Lewis, B.Sc., A.I.C.
Reginald Patrick Linstead, Ph.D., D.I.C.
Edward Hubert Lockton, B.Sc., A.R.C.S.
Charles William Long, B.Sc.
Daniel Donald Moir, B.Sc.
Ganesh Chandra Moitra, B.Sc.
Rt. Hon. Sir Alfred Moritz Mond, Bart., M.P.
Matthew Morris.
Masuo Murakami, M.Sc.
Roger Saxon Nickalls.
Shintaro Ogawa.
Mary Alice Marcia Penrose, B.Sc.
Eric Charles Pickering, Ph.D., B.Sc., A.I.C.
Stanley Ernest Pusey.
Mysore Guru Srinivasa Rao.
Alfred Leonard Read, B.Sc.
Alexander Robertson, M.A., B.Sc., Ph.D.
Sydney William Rowell, B.A.
Bernard Charles Saunders, B.A.
Maurice Schofield, B.A., B.Sc.
Robert Kenworthy Schofield, M.A., Ph.D.
Florence Ruth Shaw, B.Sc.
Rodney Thomas Shepherd, B.A.
Isaac Silberman.
Walter Lewis Lee Smith, B.Sc., A.I.C.
Percy Henry Snow.
Kenneth Spedding.
Ronald Speight.
Robert Spence, B.Sc.
Allan Ramsay Stark, B.Sc., A.I.C.
Alfred Raymond Steele, B.Sc.
Mary Elizabeth Stevens.
Frederick Robert Storrie, B.Sc., A.I.C.
Charles William Herbert Story, M.Sc.Tech.
Richard Arthur Beater Tapley, B.A., B.Sc.
Arthur Turner, B.Sc., A.I.C.
Cyril Joseph Virden, B.A.
Robert Bruce Walker, M.A.
Gilbert Oakley Ward, A.B.
Francis John Watson, M.A., M.Sc.
Albert Greville White, B.Sc., A.I.C.
Edmund White.
Robert Scott Wishart, M.A., D.Sc.
Norman Edward Wood, B.Sc.
Lakshmi Narayan Yadava, M.Sc.
Ryo Yamamoto.

The following papers were read:

"The mechanism of the reaction between a carboxylic ester and a Grignard reagent." By D. R. Boyd and H. H. Hatt.

"The production of fog in the neutralisation of alkali with hydrogen halides." By H. O. Askew.

"Constituents of *Myopurum laetum*, Forst. (the "Ngaio"). Part II. Hydrogenation of ngaione and ngaiol, and dehydration of ngaiol." By F. H. McDowall.

ANNUAL GENERAL MEETING

The Annual General Meeting will take place on Thursday, March 24th, 1927, at 4 p.m., when the President, Professor H. Brereton Baker, C.B.E., D.Sc., F.R.S., will deliver his address.

ANNIVERSARY DINNER.

The Anniversary Dinner of the Society will be held at the Hotel Victoria, King Edward VIIth Rooms, Northumberland Avenue, W.C. 2, on Thursday, March 24th, 1927 (the day of the Annual General Meeting), at Seven for Half-past Seven o'clock.

The Presidents of the Belgian, Dutch, French, German, and Italian Chemical Societies have been invited by the Council to the Dinner, and it is hoped that there will be a large and representative gather of Fellows present.

Tickets, price Twelve Shillings and Sixpence (12*s.* 6*d.*) each, including gratuities to waiters, can be obtained from the Assistant Secretary, Chemical Society, Burlington House, Piccadilly, W. 1. A remittance for the number of tickets required, made payable to S. E. Carr, must accompany each application.

LIST OF FELLOWS, 1927.

It has been decided to print the List of Fellows for 1927 and to supply the List to those Fellows who make application to the Assistant Secretary by July 31st, 1927.

List of Papers, or Abstracts thereof, received between January 20th and February 3rd, 1927. (This List does not include the titles of papers, or abstracts thereof, which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"The constituents of the cell-wall of the flax fibre." By A. E. Cashmore.

"Heterocyclic organic compounds of arsenic. Part I. The action of chloroacetamide on 3 : 4-diaminophenylarsinic acid." By A. J. Ewins, G. Newbery, and R. W. E. Stickings.

"The constitution of the disaccharides. Part XII. Lactose." By W. N. Haworth and C. W. Long.

"The labile nature of the halogen atom in organic compounds. Part XIII." By H. Graham, A. K. Macbeth, and W. B. Orr.

"Derivatives of 2-phenyl-1 : 3-benzdithiole." By W. R. H. Hurtley and S. Smiles.

"The molecular conductivity of cadmium iodide in acetonitrile." By F. K. V. Koch.

"The influence of groups and associated rings on the stability of certain heterocyclic ring systems. Part I. The substituted glutarimides." By S. S. G. Sircar.

"Apparatus for the determination of viscosities under various conditions, and discussion of the errors due to velocity changes in the moving liquid, surface tension, and air-buoyancy." By E. Masters and A. E. Goddard.

"Studies of aromatic thionyl and chlorothionyl derivatives. Part II. 1 : 2-Thionyldihydroxyanthracene and 2 : 3-thionyldihydroxyanthracene." By A. GREEN.

"The properties of conjugated compounds. Part II. Addition to butadiene esters." By E. H. FARMER and A. T. HEALEY.

"A note on the properties of malonic anhydride (carbon suboxide) C_3O_2." By M. J. EDWARDS and J. M. WILLIAMS.

"A new synthesis of oxyberberine and a synthesis of palmatine." By R. D. HAWORTH, J. B. KOEPFLI, and W. H. PERKIN.

"Melezitose and turanose." By G. C. LEITCH.

"Note on the preparation of 2-methylacenaphthpyridine." By J. STEWART.

"Reduction of nitroaromatic compounds by sugars: constitution of azoxy- and azo-compounds." By T. C. CHAUDHURI.

"Studies of electrolytic polarisation. Part VI. Electro-deposition potentials of alloys of zinc with iron, cobalt, and nickel." By S. GLASSTONE.

"The stereochemistry of the hydronaphthalenes. Part II. Decahydro-β-naphthoic acid and its optical resolution." By B. BEILENSOHN and F. W. KAY.

"The isomerism of the oximes. Part XXIX. Isomeric *p*-nitrobenzyl- and methyl-ethers of some aldoximes." By O. L. BRADY and L. KLEIN.

"The decomposition of carbon monoxide in the corona due to alternating electric fields. Part II." By R. W. LUNT and R. VENKATESWARAN.

"The properties of the chlorides of sulphur. Part I. Freezing points." By T. M. LOWRY, L. P. MCHATTON, and G. G. JONES.

"The vapour pressure of intensively-dried nitrogen tetroxide." By J. W. SMITH.

"The action of nitric acid on unsaturated hydrocarbons. The action of nitric acid on acetylene and ethylene." By P. V. MCKIE.

"Molybdenyl salts and the co-ordination number of oxygen." By W. WARDLAW and R. L. WORMELL.

"The isomerism of the oximes. Part XXX. The preparation of *o*-methoxybenzaldoxime from bisnitrosyl-*o*-methoxybenzyl." By O. L. BRADY and C. L. BENNETT.

"Studies in polymerisation. Part I. 2 : 3 : 4-Trimethyl-*l*-arabonolactone." By H. D. K. DREW and W. N. HAWORTH.

"On the photobromination of *cyclo*hexane." By B. J. WOOD and E. K. RIDEAL.

"A method for the determination of total carbon in the soil solution." By C. F. FLINT.

"A method for the determination of carbon dioxide in the soil solution." By C. F. FLINT.

"1-Methoxy-1'-carboxy-diphenyl and its demethylation with thionyl chloride." By H. G. RULE and E. BRETSCHER.

"Optical activity and the polarity of substituent groups. Part VII. *sec.*-β-Octyl hydrogen terephthalate and the isomeric *sec.*-β-octyl chlorobenzoates." By H. G. RULE, T. R. PATERSON, and A. H. NUMBERS.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. British Chemicals, their manufacture and uses: being the official directory of the Association of British Chemical Manufacturers. London 1927. pp. 242. (*Reference.*) 10*s.* 6*d.* net.

From the Publishers: Messrs. Ernest Benn.

CRAMER, MARC. Les sucres et leurs dérivés. Paris 1927. pp. xiv + 354. ill. 28 *fr.* (*Recd.* 9/2/27.)

From the Publishers: MM. Gaston Doin et Cie.

DEWAR, SIR JAMES. Collected papers. Edited by LADY DEWAR [and others]. With two supplementary papers not heretofore published. 2 vols. Cambridge 1927. pp. xxii + 674, x, 675 to 1490. ill. 84*s.* net. (*Recd.* 21/2/27.) From Lady Dewar.

DOOTSON, FREDERICK WILLIAM, and BERRY, ARTHUR JOHN. First principles of chemistry. Cambridge 1927. pp. viii + 340. ill. 6*s.* net. (*Recd.* 26/1/27.)

From the Syndics of the Cambridge University Press.

GROSSFELD, JOHANN. Anleitung zur Untersuchung der Lebensmittel. Berlin 1927. pp. xii + 410. ill. *M.* 22·50. (*Recd.* 9/2/27.) From the Publisher: Herr Julius Springer.

INSTITUT INTERNATIONAL DE CHIMIE SOLVAY. Deuxieme Conseil de Chimie tenu a Bruxelles du 16 au 24 Avril 1925. Structure et activité chimiques. Rapports et discussions. Paris 1926. pp. xiv + 672. ill. (*Reference.*) 96 *fr.* From Mr. J. Pryce Jones.

MACLEAN, HUGH, and MACLEAN, IDA SMEDLEY. Lecithin and allied substances. The lipins. [2nd] edition. London 1927. pp. viii + 220. 10*s.* 6*d.* net. (*Recd.* 9/2/27.)

From the Publishers: Messrs. Longmans, Green & Co.

MENDELÉEFF, DMITRI IVANOVICH. The law of periodicity. (Classics of Natural Science, Vol. 15.) Moscow 1926. pp. viii + 256. ill. [In Russian.] (*Recd.* 6/1/27.)

From Professor B. N. Menschutkin.

MENSCHUTKIN, BORIS NIKOLAEVITSCH. Carbocyclic compounds Leningrad 1926. pp. viii + 388. [In Russian.] (*Recd.* 6/1/27.)
From the Author.

ODDO, GIUSEPPE. Trattato di chimica inorganica. Palermo 1925. pp. xvi + 868. ill. *L.* 75. (*Recd.* 18/1/27.)
From the Author.

SÃO PAULO. *Faculdade de Medicina.* Annaes. Vol. I. São Paulo 1926. pp. xx + 384. ill. (*Reference.*)
From the Faculty.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS. Decennial Index to The Analyst. Vols. XLI–L (1916–1925). Compiled by M. B. ELLIOTT. Cambridge [1926]. pp. 354. (*Reference.*)
From the Council.

II. *By Purchase.*

CELLULOSECHEMIE. Wissenschaftliche Beiblätter zu der Zeitschrift "Der Papier-Fabrikant." Year VII, etc. Berlin 1926 +. (*Reference.*)

CHIMIE ET INDUSTRIE. Dix ans d'efforts scientifiques et industriels. 1914–1924. 2 vols. Paris [1926]. pp. xxxii + 1552, vi + 1508. ill. (*Reference.*)

DOYLE, AIDA M. [Editor.] Digest of patents relating to coal-tar dyes and allied compounds. United States patents issued prior to January 1, 1924. Easton, Pa. 1926. pp. viii + 586. (*Reference*). 90*s.* net.

FISCHER, JOSEPH. Die Zerstäubungserscheinungen bei Metallen unter besonderer Berücksichtigung der mechanisch-thermischen Zerstäubung und der elektrischen Stoffverdampfung. (Fortschritte der Chemie, Physik und physikalischen Chemie, Vol. XIX.) Berlin 1927.

GARROD, ARCHIBALD EDWARD. Inborn errors of metabolism. 2nd edition. London 1923. pp. viii + 216. 7*s.* 6*d.* net. (*Recd.* 28/1/27.)

GATTERMANN, LUDWIG. Die Praxis der organischen Chemikers. 20th edition. Edited by HEINRICH WIELAND. Berlin 1927. pp. xii + 382. ill. *M.* 15. (*Recd.* 5/2/27.)

HAWK, PHILIP BOUVIER, and BERGEIM, OLAF. Practical physiological chemistry. 9th edition. Philadelphia 1926. pp. xviii + 932. ill. 28*s.* net. (*Recd.* 28/1/27.)

KAYE, GEORGE WILLIAM CLARKSON. High vacua. London 1927. pp. xii + 176. ill. 10*s.* 6*d.* net. (*Recd.* 28/1/27.)

KOLLOIDCHEMISCHE TECHNOLOGIE. Ein Handbuch kolloidchemischer Betrachtungsweise in der chemischen Industrie und Technik. Edited by RAPHAEL ED. LIESEGANG. Parts I–VI. Dresden 1926–27. *M.* 5 per part. (*Recd.* 10/2/27.)

MICHAELIS, LEONOR. Hydrogen ion concentration: its significance in the biological sciences and methods for its determinations. Vol. I. Authorised translation from the 2nd . . . German edition. By WILLIAM A. PERLZWEIG. Baltimore 1926. pp. xiv + 300. ill. 22*s*. 6*d*. net. (*Recd*. 1/2/27.)

OSTWALD, WILHELM. Lebenslinien: eine Selbstbiographie. Vols. I and II. Berlin 1926–7. pp. viii + 268, xii + 446. ill. *M*. 17·50. (*Recd*. 10/2/27.)

RIDEAL, ERIC KEIGHTLEY, and TAYLOR, HUGH STOTT. Catalysis in theory and practice. [2nd edition.] London 1926. pp. xvi + 516. ill. 20*s*. net. (*Recd*. 1/2/27.)

SCHULTZ, GUSTAV. Die Chemie des Steinkohlenteers mit besonderer Berücksichtigung der künstlichen organischen Farbstoffe. 4th edition. Vol. I. Edited by ERWIN FERBER. Braunschweig 1926. pp. viii + 568. ill. *M*. 42·50. (*Recd*. 10/2/27.)

STAIN TECHNOLOGY. Published by the COMMISSION ON STANDARDISATION OF BIOLOGICAL STAINS. Vol. I, etc. Geneva, N.Y. 1926 +. (*Reference*.)

TAGUE, EDGAR L. Casein: its preparation, chemistry, and technical utilization. [New York] 1926. pp. vi + 218. ill. 17*s*. net. (*Recd*. 28/1/27.)

WAITE, ARTHUR EDWARD. The secret tradition in alchemy: its development and records. London 1926. pp. xxii + 416. 15*s*. net. (*Recd*. 28/1/27.)

WAKSMAN, SELMAN A., and DAVISON, WILBURT C. Enzymes: properties, distribution, methods, and applications. [Baltimore, Md.] 1926. pp. xiv + 364. ill. 25*s*. net. (*Recd*. 28/1/27.)

III. *Pamphlets*.

DEY, BIMAN BIHARI. Presidential address. (From the *Proc. 13th Indian Science Congress, Section of Chemistry*.) 1926.

DONALD, ROBERT. A Wassermann micro-technique needing only occasional titration of the complement. (From the *Brit. J. Derm. Syphilis*, 1923, **35**.)

GIMINGHAM, CONRAD THEODORE, MASSEE, A. M., and TATTERSFIELD, FREDERICK. A quantitative examination of the toxicity of 3 : 5-dinitro-*o*-cresol and other compounds to insect eggs, under laboratory and field conditions. (From the *Ann. Applied Biol*., 1926, **13**.)

GOVERNMENT LABORATORY. Report of the Government Chemist . . . for the year ending 31st March, 1926, etc. London 1926 +.

INTERNATIONAL CONFERENCE ON THE BIOLOGICAL STANDARDIZATION OF CERTAIN REMEDIES, Second. (From the *U.S. Public Health Reports*, 1926, **41**.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, March 3rd, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death on February 17th, of Mr. Montague Williams, who was elected a Fellow on February 15th, 1923.

The following list of nominations for vacant places on the Council was read from the Chair:

Vice-President who has filled the office of President (one vacancy):
Harold B. Dixon.

Vice-Presidents who have not filled the office of President (two vacancies):
G. G. Henderson and Arthur Smithells.

Ordinary Members of Council:

(*a*) Town Members, *i.e.*, those resident within 50 miles of Charing Cross (three vacancies):
E. R. Bolton, J. C. Drummond, and J. F. Spencer.

(*b*) Country Members, *i.e.*, those resident beyond 50 miles from Charing Cross (three vacancies):
M. P. Applebey, J. E. Coates, and E. K. Rideal.

The following were formally admitted Fellows of the Chemical Society: R. T. Shepherd, G. B. Scott, F. J. Watson, N. E. Wood.

Certificates were read for the first time in favour of:

Robert Andrew, Old Park Road, Belfast.
William Barklamb, 48, Brookmill Road, Deptford, S.E. 13.
Fritz Alfred Bate, B.Sc., 50, Eastwood Lane, Westcliff-on-Sea.
William Bradley, M.Sc., 130, New Bold Street, Leigh, Lancs.
Charles Forrester, F.I.C., Indian School of Mines, Dhanbad, India.
Gerald Charles Leake Griffin, Ministry of Labour, Whitehall, S.W. 1.
James Charles Harral, 201, Bradford Road, Batley.
Norman Holt Hartshorne, M.Sc., A.I.C., 40, Druslyn Road, West Cross, Swansea.
Jason Louis Edward Lewkowitsch, A.R.C.S., 71, Priory Road, N.W. 6.
Ernest Matthews, M.Sc., A.R.C.S., 44, Badminton Road, Balham, S.W. 12.
John Tomlinson, B.Sc.Tech., 33, Windsor Road, Levenshulme, Manchester.

The following papers were read :

"The decomposition of carbon monoxide in the corona due to alternating electric fields. Part II." By R. W. LUNT and R. VENKATESWARAN.

"The properties of the chlorides of sulphur. Part I. Freezing-points." By T. M. LOWRY, L. P. MCHATTON, and G. G. JONES.

Ordinary Scientific Meeting, Thursday, March 17th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
Arthur William Crossley	Dec. 4th, 1890.	Mar. 5th, 1927.
James Alfred Kendall	Dec. 17th, 1874.	Mar. 1st, 1927.
Edmund Felix Mondy	Dec. 17th, 1879.	April 20th, 1926.
Ira Remsen (Honorary Fellow)	Jan. 20th, 1898.	Mar. 1927.

and stated that the following resolution had been passed at the Council Meeting held that afternoon :

> The Council desires to express, on behalf of the general body of Fellows, its deep sorrow and sense of loss in the death of Dr. Arthur W. Crossley. Since his election 36 years ago, Dr. Crossley has served on the Council for a period of 23 years, filling with conspicuous zeal and ability the offices of Secretary, Foreign Secretary, and President.
>
> In offering to Mrs. Crossley its sincere sympathy in her great loss, the Council desires to record its high appreciation of the distinguished services rendered by Dr. Crossley not only to the Society, but to the science of Chemistry and its application to industry.

The company present expressed their concurrence in this resolution by rising from their places. The Society was represented at the funeral on March 9th by Professor H. B. Dixon, other present and past members of Council, and the Assistant Secretary.

The PRESIDENT announced that in accordance with Bye-Law II, Professor Dr. Richard Willstätter, of Munich, was proposed by the Council as an Honorary Fellow of the Society, and that a ballot for his election would be held at the next Ordinary Scientific Meeting on April 7th.

Certificates were read for the first time in favour of:

Keith Lester Beak, 25, Chadwick Road, Leytonstone, E. 11.
Thomas Eric Ellison, 22, Kelvin Parade, Belfast.
Thomas Alfred Jenkinson, B.Sc., 5, Glebe Street, Marsh, Huddersfield.
Louis Arnold Jordan, D.Sc., A.R.C.S., F.I.C., 14, Parklands, Surbiton.
Alfred William Mond, B.A., 104, Eaton Place, S.W. 1.
John Hopkinson Parker, 57, Grafton Road, Keighley.
Arthur Shortt, B.Sc., St. Andrews, Clayton Road, Newcastle-on-Tyne.
Robert Louis Wormell, Coniston, Stoke Park, Coventry.

The following papers were read:

"Tetrachloro-(triaminopropane-γ-monohydrochloride)-platinum, a new type of optically active complex salt." By F. G. MANN.

"The activation of wood charcoal by progressive oxidation in relation to bulk density and iodine adsorption." By A. B. P. PAGE.

"The parachor and chemical constitution. Part V. Evidence for the existence of singlet linkages in the pentachlorides of phosphorus and antimony." By S. SUGDEN.

LIST OF FELLOWS, 1927.

It has been decided to print the List of Fellows for 1927 and to supply the List to those Fellows who make application to the Assistant Secretary by July 31st, 1927.

List of Papers, or Abstracts thereof, received between February 17th and March 17th, 1927. (This List does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"Acid and salt effects in catalysed reactions. Part VII. The tridimensional co-ordination of catalytic variables. Relations between the data for pure acids and the corresponding minimum velocity mixtures." By H. M. DAWSON.

"The gelatin precipitation test for tannins." By A. E. JONES.

"The solubility of potassium ferrocyanide in water at temperatures up to 25° C." By R. H. VALLANCE.

"Reactions of incandescent tungsten with nitrogen and with water vapour." By C. J. SMITHELLS and H. P. ROOKSBY.

"The nature of the alternating effect in carbon chains. Part XVIII. Mechanism of exhaustive methylation and its relation to anomalous hydrolysis." By W. HANHART and C. K. INGOLD.

"The constitution of certain salts and acids in solution by observations of critical solution temperatures." By S. R. CARTER and N. J. L. MEGSON.

"A micro-method for the estimation of nitrate in soil solutions and extracts." By C. F. FLINT.

"The determination of carbonyl in aldehydes and ketones." By G. W. ELLIS.

"A note on the Schwartzchild law with reference to photographic spectrophotometry." By F. SIMEON.

"New fluorides of selenium." By E. B. R. PRIDEAUX and C. B. COX.

"Investigations in the diphenyl series. Part V. Derivatives of 4-aminodiphenyl and diphenic acid." By F. BELL and P. H. ROBINSON.

"αβ-Dichloro β-bromovinyl ethyl ether." By I. A. SMITH.

"Studies of precipitated solids (especially $SrSO_4$ and $CaSO_4$)." By P. P. VON WEIMARN.

"The optically active diphenylhydroxyethylamines and *iso*hydrobenzoins. Part I." By J. READ and C. C. STEELE.

"Higher substitution products of 4-aminodiphenyl." By H. A. SCARBOROUGH and W. A. WATERS.

"The iodination of *o*-nitrophenol." By H. H. HODGSON.

"The interaction of ethyl acetoacetate with distyryl ketones. Part III. *ortho*Hydroxychlorodistyryl ketones." By I. M. HEILBRON and R. HILL.

"Jackson and White's synthesis of phenanthrene." By J. KENNER and J. WILSON.

"The basic character of the acetxylides and its influence on the course of their substitution." By H. E. DADSWELL and J. KENNER.

"The dicarbazyls. Part II. 9 : 9′-Dicarbazyl and its halogen derivatives." By J. MCLINTOCK and S. H. TUCKER.

"The influence of groups and associated rings on the stability of certain heterocyclic ring systems. Part II. The substituted succinimides." By S. S. G. SIRCAR.

"The influence of groups and associated rings on the stability of certain heterocyclic ring systems. Part III. Substituted paraconic acids." By S. S. G. SIRCAR.

"The interaction of alkali sulphites with some halogeno-compounds, and the optical resolution of α-phenylpropanesulphonic acid." By E. B. EVANS, E. E. MABBOTT, and E. E. TURNER.

"The periodic electro-deposition of metals through secondary reaction." By E. S. HEDGES.

"Piperidine as a general reagent for the determination of con-

stitution of halogeno-nitro-compounds. The nitration of 4 : 4′-dihalogeno-diphenylmethane and *s*-diphenylethane." By R. J. W. Le Fèvre and E. E. Turner.

"The laws of sympathetic vibrations. Unisons and octaves." By A. T. S. Clark.

"Some experiments with 1 : 8-naphthalyl chloride." By W. Davies and G. W. Leeper.

"The disulphonation of *m*-dichlorobenzene and of *s*-trichlorobenzene." By W. Davies and H. G. Poole.

"The recovery of pinene from its nitrosochloride." By J. C. Earl and J. Kenner.

"Researches on residual affinity and co-ordination. Part XXIX. Cupric salts stabilised by ethylenediamine." By G. T. Morgan and F. H. Burstall.

"The purification of acetic acid. The estimation of acetic anhydride in acetic acid." By K. J. P. Orton and A. E. Bradfield.

"The chlorination of anilides. The directing influence of the acylamino-group." By K. J. P. Orton and A. E. Bradfield.

"The constitution of sulphur dioxide in solution. Part I. The influence of hydrochloric acid on the distribution ratio of sulphur dioxide." By S. R. Carter and A. E. T. Neale.

"The constitution of sulphur dioxide in solution. Part II. The influence of temperature on the distribution ratio of sulphur dioxide." By S. R. Carter and A. E. T. Neale.

"The solubility of sulphur dioxide in water, chloroform, and westron." By S. R. Carter and A. E. T. Neale.

"Acid and salt effects in catalysed reactions. Part VIII. The determination of hydrolytic velocity coefficients from *iso*-catalytic data. Reaction velocities in buffer solutions and compound catalytic catenaries." By H. M. Dawson.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, MAY 5TH, 1927.

Andrew, Robert, Old Park Road, Belfast. British. Pharmaceutical Chemist. Member of the Pharmaceutical Society of Northern Ireland. Licentiate of the Pharmaceutical Society, Irish Free State. No published communications. Interest in current advances in chemistry, particularly in relation to pharmacy and medicine. (*Signed by*) Theo. Harper, James Dundee, D. Hughes, P. J. Thompson, D. P. Woosley.

Barklamb, William, 48, Brookmill Road, Deptford, S.E. 13. English. Asst. Chemist. Student at the Sir John Cass Technical Institute (Adv.

Organic Chem.). Wish to keep in touch with the latest advances in Chemistry and would appreciate the use of the Library. (*Signed by*) E. de Barry Barnett, W. V. Lloyd, J. L. Wiltshire.

BATE, FRITZ ALFRED, 50, Eastwood Lane, Westcliff-on-Sea, Essex. British. Student. B.Sc., 2nd Hons., London. 4 Years East London College. 1 Year research, Battersea Polytechnic. (*Signed by*) J. Kenyon, F. Bell, Henry Phillips.

BEAK, KEITH LESTER, 25, Chadwick Road, Leytonstone, E. 11. British. Assistant in Engineer-in-Chief's G.P.O. Test Section, Chemical Dept., Studd St., N. 1. (*Signed by*) Bernard W. Crutchlow, W. Williamson, A. H. Durrant.

BRADLEY, WILLIAM, 130, New Bold Street, Leigh, Lancs. British. Research Student. Graduated 1924. B.Sc. (Hons.), University of Manchester. M.Sc. Degree, 1925, University of Manchester. "Hydrolytic Fission of some Substituted Dibenzoylmethanes," *J.C.S.*, 1926, 2356. (*Signed by*) Robert Robinson, Arthur Lapworth, Frederick Challenger.

BUNCE, EDWIN HERBERT, 37, Northcote Road, Walthamstow, Essex. British. Works Chemist to Grays, Colors, & Dyes, Ltd. A.I.C. Formerly for 5 years in the laboratory of Dr. Bernard Dyer. (*Signed by*) Bernard Dyer, George Senter, George Taylor, F. J. Thorneycroft.

BURTON, DAVID HENRY, 49, Rayleigh Road, Wimbledon, S.W. 19. British. Research Assistant. B.Sc. (1st Class Hons., London). A.R.C.S. A.I.C. (*Signed by*) C. S. Gibson, J. Davidson Pratt, M. A. Whiteley.

CAMERON, CHARLES MCKENLEY, 146, Whalley Road, Clayton-le-Moors, Accrington. British. Chemist and Druggist. Member of the Pharmaceutical Society. 1915–1919, Lancashire and Cheshire Institute Course (certificates with honours). 1920–1921, Student, Manchester College of Pharmacy (certificate of proficiency). 1922 onwards, giving instruction to students preparing for the Chemist and Druggist Qualifying Examination, Part I (Chemistry and Physics). Completed the Major Course for the Pharmaceutical Chemists Diploma. Present reading up Metallurgical Chemistry and the Analysis of Food and Drugs. (*Signed by*) H. Brindle, J. W. Bell, Jules Cofman Nicoresti.

CHADWICK, RICHARD, 133, Whitefriar's Avenue, Wealdstone, Middlesex. British. Natural Science Tripos, Part II, Chemistry, 1925, 2nd Class. B.A., Honours, Cambridge, 1925. Research work in Metallurgy under Mr. C. T. Heycock, F.R.S., for 18 months. (*Signed by*) A. J. Berry, Hamilton McCombie, F. W. Dootson.

CHRISTY, RONALD KINGTON, 3, Crieff Road, Wandsworth, S.W. 18. British. University Demonstrator. B.Sc. (Lond.), 2nd Class Honours in Chemistry. Demonstrator in Biochemistry. (*Signed by*) A. J. Allmand, Samuel Smiles, H. Gordon Reeves.

COPLEY, EDGAR DAWN, Bulawayo, S. Rhodesia. British. Works Chemist. Degrees: B.Sc. (South Africa) (Physics and Chemistry). B.A. and B.Sc. (Oxon.) (Chemistry). (*Signed by*) J. L. Wiltshire, M. Farrow, J. K. Marsh, M. P. Applebey, S. G. P. Plant, J. M. Gulland, E. Hope.

ELLISON, THOMAS ERIC, 22, Kelvin Parade, Belfast, N.I. English. University Assistant in Chemistry. Assistant in Chemistry in the Queen's University of Belfast, 1924–1927. (*Signed by*) A. W. Stewart, H. Graham, W. H. Crowe.

FORRESTER, CHARLES, Indian School of Mines, Dhanbad, Bihar and Orissa, India. British. Professor of Chemistry and Assaying, Indian School of Mines, Dhanbad, Bihar and Orissa, India, E.I.R. Associate Heriot-Watt College, Edinburgh. Fellow of the Institute of Chemistry. Several years

Lecturer in Chemistry and Assaying at the Heriot-Watt College, Edinburgh. (*Signed by*) John Dall, J. J. Blackie, Eric Knott.

GRIFFIN, GERALD CHARLES LEAKE, Ministry of Labour, Montagu House, Whitehall, S.W. 1. British. Civil Servant. Foundation Scholarship in Exp. Sc., Trinity College, Dublin. Senior Moderatorship, B.A., Large Gold Medal, Exp. Sc. (Chem. and Phys.), Dublin Univ. I desire to keep in touch with the progress of Chemistry. (*Signed by*) Sydney Young, Emil. A. Werner, Kenneth C. Bailey, A. G. G. Leonard, James Bell.

GURNEY, JOHN, Walsingham Abbey, Norfolk. British. Research Student. Part I, Honour School of Chemistry, Oxford, 1926. (*Signed by*) W. H. Perkin, S. G. P. Plant, J. Masson Gulland.

HARRAL, JAMES CHARLES, 201, Bradford Rd., Batley, Yorks. English. Analytical Chemist (Assistant). With Messrs. F. W. Richardson and A. Jaffé, Public Analysts, etc., Bradford. Over five years' pupilship with Messrs. Richardson and Jaffé, with whom he is now Assistant. (*Signed by*) Frederick William Richardson, Adolph Jaffé, Herbert Hodgson.

HARTSHORNE, NORMAN HOLT, 40, Druslyn Road, West Cross, Swansea. British. Assistant Lecturer in Inorganic and Physical Chemistry, University College, Swansea. Late Demonstrator in Inorganic and Physical Chemistry, Bedford College, University of London. M.Sc. (B'ham.). A.I.C. Published work (in *J.C.S.*): "System Ferric Oxide–Phosphoric Acid–Water," 1923, **123**, 2223; "Apparatus for Viscosimetric Determination of Transition Points," 1924, **125**, 2096; "System Ferrous Oxide–Phosphoric Acid-Water," 1926, 363. (*Signed by*) J. E. Coates, L. E. Hinkel, E. E. Ayling.

HATFIELD, WILLIAM HERBERT, Muswell Lodge, Brincliffe Crescent, Sheffield. British. Principal of the Brown Firth Research Laboratories, Princess St., Sheffield. D.Met. (Sheffield), F.Inst.P. M.Inst.Mech.E. Papers given to Royal Society, Iron and Steel Inst., Inst. of Metals, Inst. Mech. Eng., etc. (*Signed by*) Ulick R. Evans, Cecil H. Desch, W. P. Wynne.

HOOLEY, LEONARD JOSEPH, 11, Newhouse Road, Grangemouth, Stirlingshire. English. Chemist. B.A. (Cantab.). Natural Science Tripos, Part II, Chemistry, 2nd Class, 1920. A.I.C. (*Signed by*) W. J. Pope, W. H. Mills, John Thomas.

HOWARD, GEORGE ROBERT, 32, Gilpin St., Peterborough. British. Teacher of Chemistry (Junior Science Master, Skipton Grammar School). 1st Class Hons. B.Sc. (Honours School of Chemistry, Univ. of Sheffield). Desirous of receiving Journal and keeping in touch with recent research. (*Signed by*) W. P. Wynne, F. G. Tryhorn, G. M. Bennett, Arthur W. Chapman, W. F. Wyatt.

JENKINSON, THOMAS ALFRED, 5, Glebe St., Marsh, Huddersfield. English. Research Student and Part-time Teacher. B.Sc. (London). Diploma in Chemistry, Hudd. Tech. College. Laboratory Assistant at British Dyestuffs Corporation, Ltd., 1918–1921. Day-student at Huddersfield Technical College, 1921–1927. (*Signed by*) Herbert H. Hodgson, L. Gordon Paul, James Bruce.

JORDAN, LOUIS ARNOLD, 14, Parklands, Surbiton. British. Director Paint and Varnish Research Assocn. D.Sc. (London). A.R.C.Sc. (London). D.I.C. F.I.C. *J.C.S.*, 1915, p. 387. (*Signed by*) Jocelyn Thorpe, James C. Philip, H. F. Harwood.

KNAPP, ARTHUR WILLIAM, "Trinidad," Pine Apple Rd., King's Heath, Birmingham. British. Chief Chemist, Messrs. Cadbury Bros., Bournville. B.Sc. (Lond. and Birm.). F.I.C. M.I.Chem.E. Papers in the *Analyst*: 1909, 12; 1910, 385; 1912, 3; 1913, 102; 1919, 2; 1923, 486. Papers in

the *Journal of the Society of Chemical Industry:* Dec. 1910; 1911, 165; 1914, 158; 1915, 1121; 1918, 240T; 1924, 124T and 402R; 1925, 453T; 1926, 123T and 140T. (*Signed by*) Wm. Wardlaw, W. J. Hickinbottom, S. R. Carter, J. D. Main Smith.

LEWKOWITSCH, JASON LOUIS EDWARD, 71, Priory Rd., N.W. 6. British. Student. At present engaged in Physical Chemistry research. A.R.C.S. (*Signed by*) James C. Philip, H. J. T. Ellingham, J. H. G. Carlile.

MCGREGOR, JAMES HUTCHISON, Avenue Cottage, Alexandria, Dumbartonshire. British. Technical Chemist, The United Turkey Red Co., Ltd., Glasgow. Associate of The Royal Technical College, Glasgow (A.R.T.C.). Associate of The Institute of Chemistry (A.I.C.). Formerly Research Chemist with The British Alizarine Co., Ltd., Manchester. (*Signed by*) William M. Cumming, M. M. J. Sutherland, R. M. Caven, John A. Cranston.

MAJUMDAR, TARAK NATH, 11, Belvedere Road, Calcutta. Hindu. Health Officer, Corporation of Calcutta and Professor of Hygiene, Carmichael Medical College, Calcutta. D.P.H. D.T.M. F.R.S.E. Late Asst. Analyst, Corporation of Calcutta, 1908–11. Examiner in Hygiene and Public Health for M.B. Examination, University of Calcutta, 1913–27. Examiner in D.P.H. (Chemistry, Physics), University of Calcutta, 1921–23. Professor of Hygiene, Carmichael Medical College. (*Signed by*) Tin Kari Ghose, Chuni Lal Bose, Beni Madhub Chakravarti.

MATTHEWS, ERNEST, 44, Badminton Rd., Balham, S.W. 12. British. Demonstrator in Chemistry, Medical School, Guy's Hospital. M.Sc. A.R.C.S. D.I.C. *J.C.S.*, 1926, 2270. (*Signed by*) John H. Carlile, A. T. Healey, J. T. Evans.

MILLWARD, HERBERT JOSEPH, "Ivydene," Gravelly Lane, Erdington, Birmingham. British. Lecturer's Assistant, Birmingham University. Senior Laboratory Steward, King Edwards Grammar School, 3 years. Army Dispenser, R.A.M.C. (T.F.), 4 years. Lecturer's Assistant, Birmingham University, 7 years. I am desirous of keeping in touch with Chemical progress. (*Signed by*) W. N. Haworth, S. R. Carter, E. L. Hirst.

MOND, ALFRED WILLIAM, 104, Eaton Place, London, S.W. 1. British. Assistant Works Manager, Brunner, Mond & Co., Ltd., Northwich. B.A., Cambridge. 3 Years' research at Oxford. (*Signed by*) F. A. Freeth, F. G. Donnan, N. V. Sidgwick.

PARKER, JOHN HOPKINSON, 57, Grafton Road, Keighley, Yorks. English. Assistant Brewer and Chemist. Studied Chemistry under Mr. H. Harper, B.Sc., A.R.C.Sc., A.I.C., F.C.S.; Mr. L. M. Stockdale, B.Sc., M.Sc., F.C.S., and Mr. J. Ross-Mackenzie, F.C.S., F.R.M.S., and am desirous of receiving the publications of the Society. (*Signed by*) Herbert Hobson, Harry Harper, Leonard M. Stockdale.

RIPPON, DOROTHY MAY LYDDON, Springfield House, Abingdon, Berks. British. Research Student. B.A., Oxon. (Chemistry), Honours. (*Signed by*) W. H. Perkin, S. G. P. Plant, J. M. Gulland, E. Hope.

SHAW, OTTO LESLIE, "Betula," Park View Rd., New Eltham, S.E. 9. English. Analytical Chemist (in the employ of the Shell-Mex Oil Co., Ltd.). Delivered course of lectures on the Growth of Chemistry. (*Signed by*) George Senter, F. J. Thorneycroft, A. M. Ward, Samuel Sugden.

SHORTT, ARTHUR, St. Andrews, Clayton Rd., Newcastle-on-Tyne. British. Industrial Chemist. B.Sc. (Hons.), Durham. Barrister-at-Law. 4½ Years' Research Chemist, United Alkali Co., Ltd. Now Pelaw Main Colliery Co. (*Signed by*) P. Phillips Bedson, J. A. Smythe, P. L. Robinson.

TOMLINSON, JOHN, 33, Windsor Road, Levenshulme, Manchester. British.

Research Student (Geology Department of Manchester University). B.Sc. (Tech.), Honours, Fuel. (*Signed by*) W. H. Brindley, T. K. Walker, John K. Wood.

TYLER, ALLAN GEORGE, 48, Bentley Street, Lockwood, Huddersfield. British. Research Student. Student, Leeds University, 1923–26. Hons. B.Sc., Colour Chemistry, 1926. Draper's Co.'s Research Scholarship, Huddersfield Technical College, 1926–. (*Signed by*) P. K. Dutt, E. Phillis, G. V. Hall.

USHER, ALBERT DENNY, 106, Bolingbroke Grove, S.W. 11. British. Assistant Schoolmaster. B.Sc. (London). Post-graduate Student of Chemistry. Wishing to keep in touch with the progress of the subject. (*Signed by*) J. W. Cook, E. de Barry Barnett, P. C. L. Thorne.

WARD, CARL ROMEN, Woodcroft, Newburn, Northumberland. English. Student (Emmanuel College, Camb.). Intends to be teacher in Chemistry. B.A. (Cambridge). Nat. Science Tripos, Pt. I. At present training for Diploma in Education with Endorsement in Chemistry. (*Signed by*) John S. Bousfield, R. G. W. Norrish, F. W. Dootson.

WINGFIELD, CHARLES BARNETT, 36, Clarendon Gdns., Wembley, Middlesex. British. Senior Asst. Chemist with Messrs. A. Duckham & Co., Ltd., Oil Refiners and Lubricant Manufacturers, 6, Broad Street Place, E.C. 2. Fourteen years' experience of practical laboratory work with the above firm. Associate Member Institution Petroleum Technologists. (*Signed by*) A. Duckham, Robert Redwood, S. Bowrey.

WORMELL, ROBERT LOUIS, "Coniston," Stoke Park, Coventry. English. Research Chemist. Part-time Demonstrator in Chemistry, Birmingham University (1925–27). *J.C.S.*, 1924, **125**, 2370; 1927, 130. (*Signed by*) Wm. Wardlaw, F. W. Pinkard, H. M. Spittle.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ABDERHALDEN, EMIL. Handbuch der biologischen Arbeitsmethoden. Abt XI. Chemische, physikalische und physikalisch-chemische Methoden zur Untersuchung des Bodens und der Pflanze, Teil 3, Heft. v. Berlin 1927. pp. 715 to 864. ill. *M.* 7.20. (*Recd.* 2/3/27.)

From the Publishers: Herren Urban & Schwarzenberg.

AMERICAN MEDICAL ASSOCIATION. Annual Reports of the Chemical Laboratory. Vol. 17–18, 1924–25. Chicago. (*Reference.*) $1.25.

From the Laboratory.

INDUSTRIAL CHEMIST and Chemical Manufacturer. Vol. 3, etc. London 1927 +. (*For circulation.*)

From the Society of Dyers and Colourists.

JOURNAL OF POMOLOGY AND HORTICULTURAL SCIENCE. Vol. V, etc. London 1925 +. (*Reference.*)

From the Bureau of Chemical Abstracts.

KUHLMANN. Cent ans d'industrie chimique. Les établissements Kuhlmann 1825–1925. Paris 1926. pp. 138. ill. (*Recd.* 17/2/27.)

From the Director.

NATUURWETENSCHAPPELIJK TIJDSCHRIFT. Tolk van Afdeelingen I en III van het Vlaamsch Natuur- en Geneeskundig Congres. Year VIII, etc. Antwerpen 1926 +. (*Reference.*)

From the Secretary.

SCHIMMEL & Co. Bericht über ätherische Öle, Riechstoffe usw. 12 vols. Miltitz bez. Leipzig 1914–15, 1918–26. (*Reference.*)

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

ANNIVERSARY DINNER.

THE Anniversary Dinner of the Chemical Society was held at the Hotel Victoria (King Edward VII Rooms) on Thursday, March 24th, 1927, at 7 for 7.30 p.m., the President, Professor H. B. BAKER, C.B.E., D.Sc., F.R.S., being in the Chair. The following Fellows and Guests were present :—

Applebey, M. P.
Armstrong, H.
Armstrong, Mrs. H.
Armstrong, Miss N.
Austin, P. C.
Baker, Miss A. M.
Baker, H. Brereton, C.B.E., F.R.S., *President.*
Baker, Mrs. H. Brereton.
Baker, S.
Barger, G., F.R.S.
Baron, H.
Baron, Mrs. H.
Bedson, P. P.
Bennett, Miss D. M.
Benton, W. A.
Blackwell, F. V., C.B.E., M.C.
Blair, J. W.
Bolton, E. R., *President, Society of Public Analysts.*
Borns, H.
Bradstreet, H.
Bradstreet, Mrs. H.
Brame, J. S. S.
Bunker, S. W., D.S.O., M.C.
Burton, D. H.
Cain, Miss E.
Cain, Mrs. J. C.
Carlton, Miss M.
Carpmael, A.
Carr, F. H., C.B.E., *President, Society of Chemical Industry.*
Carr, Mrs. F. H.
Carr, S. E., *Assistant Secretary.*
Chapman, A. Chaston, F.R.S.
Chapman, Mrs. A. Chaston.
Chattaway, F. D., F.R.S.
Chemical Age.
Clifford, F. W., *Librarian.*
Coates, J. E., O.B.E.
Colles, W. M.
Colles, Mrs. W. M.
Dickes, Miss W. E.
Donnan, F. G., C.B.E., F.R.S., *Foreign Secretary.*
Druce, J. G. F.
Drummond, J. C.
Dunningham, A. C.
Durrans, T. H.
Durrans, Mrs. T. H.
Dyer, B.
Dyer, Mrs. B.
Eck, J.
Eck, Miss M. E.
Edser, E.
Ehrhardt, E. F.
Ehrhardt, Mrs. E. F.
Eldridge, A. A.
Eldridge, Mrs. A. A.
Ellingham, H. J. T.
Fargher, R. G.
Findlay, A.
Flürscheim, B.
Freeth, F. A., O.B.E., F.R.S.

Gamble, F. W.
Gamble, Mrs. F. W.
Gater, R. E.
Gerrard, W.
Gibb, Sir Alexander, G.B.E., C.B., *President, Institution of Chemical Engineers.*
Gibson, C. S., O.B.E., *Secretary.*
Goldsmith, J. N.
Gray, W. H.
Green, A. G., F.R.S.
Green, Mrs. A. G.
Greenaway, A. J.
Gregory, Sir Richard.
Hamp, Miss A. G.
Harington, C. R.
Haworth, W. N.
Heath, Sir Frank, K.C.B., *Secretary, Department of Scientific and Industrial Research.*
Henry, T. A.
Henry, Mrs. T. A.
Hewitt, J. T., F.R.S.
Hill, C. A., *Chairman, Association of British Chemical Manufacturers.*
Hinchley, J. W.
Hodgkin, A. E., M.C.
Hooper, E. Grant.
James, T. C.
Johnson, J. D.
Jowett, H. A. D.
Kenyon, J.
Lakeman, Miss E.
Lakeman, H. B.
Lambourne, H.
Lapworth, A., F R.S.
Lowndes, J.
Lowry, T. M., C.B.E., F.R.S.
Maclean, Mrs. I. S.
Marlow, G. S. W.
Masson, Irvine, M.B.E.
Matignon, C., *Société Chimique de France.*
Matthews, E.
Maxwell, L. B.
Merrin, A. C.
Merrin, Mrs. A. C.
Miall, S.
Miall, Mrs. S.
Micklethwait, Miss F. M. G., M.B.E.
Micklethwait, St. J. G.
Mitchell, A. D., *Assistant Editor.*
Mitchell, Mrs. A. D.
Morris, H. J.
Neilsen, H.
Neilsen, Mrs. H.
Nixon, I. G.
Nutland, J. H.
Orton, K. J. P., F.R.S.
Paget, H.
Paget, Mrs. H.
Partington, J. R., M.B.E.
Partington, Mrs. J. R.
Patchin, G.
Philip, J. C., O.B.E., F.R.S.
Philip, Mrs. J. C.
Pickering, E. C.
Plimmer, R. H. Aders.
Pope, Sir William J., K.B.E., F.R.S., *Past-President.*
Porritt, B. D.
Porritt, Mrs. B. D.
Press Association.
Price, T. Slater, O.B.E., F.R.S., *Secretary.*
Pyman, F. L., F.R.S.
Pyman, Mrs. F. L.
Randerson, W.
Randerson, Mrs. W.
Robertson, Sir Robert, K.B.E., F.R.S.
Robertson, Lady.
Robinson, R., F.R.S.
Robinson, Mrs. R.
Rosedale, J. L.
Rost, F. E. B.
Rowlands, M. J.
Rutherford, Sir Ernest, O.M., *President, The Royal Society.*
Schlenk, W., *President, Deutsche Chemische Gesellschaft.*
Schryver, S. B.
Sharp, T. M.
Sidgwick, N. V., F.R.S.
Smith, Clarence, *Editor.*
Smith, P. A.
Smithells, A., C.M.G., F.R.S., *President, Institute of Chemistry.*
Sodeau, W. H.
Sodeau, Mrs. W. H.
Spencer, J. F.
Spencer, L. J., F.R.S.
Spielmann, P. E.
Sugden, J. N.
Sumner, The Right Hon. Viscount, G.C.B.
Teed, F. L.

Thomas, N. Garrod.
Thompson, G. E.
Thompson, Mrs. G. E.
Thorpe, J. F., C.B.E., F.R.S., *Treasurer*.
Thorpe, Mrs. J. F.
Times.
Turner, Miss E. G.
Turner, G. W.
Voelcker, J. A.
Wagner, W. G.
Watson, H. E.
Whiteley, Miss M. A., O.B.E.
Williamson, J. W.
Williamson, Mrs. J. W.
Wood, Miss F. M.
Wynne, Miss D. P.
Wynne, W. P., F.R.S., *Past-President*.

The following is a list of the Toasts proposed :—

1. " His Most Gracious Majesty The King."
2. " Her Majesty the Queen, His Royal Highness the Prince of Wales, and the other members of the Royal Family."
3. By The Right Honourable VISCOUNT SUMNER, G.C.B. :—
" The Chemical Society," coupled with the name of the President.
4. By SIR WILLIAM J. POPE, K.B.E., LL.D., F.R.S. :—
" The Guests," coupled with the names of
   (*a*) SIR ERNEST RUTHERFORD, O.M.,
   President of the Royal Society (1662).
   (*b*) Professor CAMILLE MATIGNON,
   representing the Société Chimique de France (1857).
   (*c*) Hofrat Professor Dr. Wilhelm Schlenk, President, Deutsche Chemische Gesellschaft (1867).

After the Loyal Toasts had been honoured, VISCOUNT SUMNER proposed the Toast of " The Chemical Society "; he said :—

Mr. President, Ladies, and Gentlemen, I have the honour to propose to you the toast of " The Chemical Society " coupled with the name of the President, and I put it to you now, and if you agree with me, I hope you will honour it in the usual way. That is a toast which needs no further words in support of it, and therefore I am justified in sitting down at once. Your response is not what I expected, and I can only suppose it is due to the fact that I am a stranger here.

When the President was so good as to ask me to this feast, he mentioned quite casually that it was the custom of the Chemical Society to include among the guests some persons who were not men of science, and it was in that capacity I understood I was invited. It struck me at the time as being an excellent reason for extending your hospitality to such as I am, because, as I thought, it could not but be good for us to see chemists in their habit as they live—a most attractive way, I am sure. I must confess you are not quite what I expected, because the learning which I am quite sure is present in all of you is not in every case as ostensible as I thought it would

be. A few days later, I received a letter from him asking me to propose this toast, and then I had misgivings, for with what object could a person, who was emphatically not a man of science, be asked to address the Chemical Society? And I could only think of blind Samson being made sport of long ago.

There used to be, when I was a boy, an excellent maxim which said, "Little boys should be seldom seen and never heard." I might have understood coming here and being seen on this rare occasion, but I should not on any terms be heard at all; yet here I am, entrusted with what is almost the toast of the evening and called upon to address you. What shall I say?

I have been supplied, by the kindness of the Secretary, with a quantity of printed information. There is a Report of the Council 1926—7, and there is an account of the state of your finances, which I notice, like the national finances, are slightly on the wrong side. Then at the end there are debit and credit accounts, income and expenditure accounts, and accounts of the Research Fund and Publications Fund and the Special Publications Fund and the General Purposes Fund and sundry others. I have read this document, not without some hope that I should find in it what I should eventually say to you, but except that I have discovered the very respectable fact that this Society was founded in 1841 and has a flourishing number of Fellows—I think no fewer than 4093—and that it is the practice of members of the Society to read papers to one another, with a warning that all manuscripts must be submitted in a legible and easily read handwriting—I am afraid I did not discover very clearly what bearing that printed document had on the speech I have to deliver to you.

But sincerely I wish the prosperity, which attended you in 1841, may continue till 1941 and 2041 and similar anniversaries. I should like to say something to you about chemistry, because that is the most humorous thing I can think of doing: to lay before a learned Society in my own original language my views on your science. I should think that must be full of fun, but whether, as they say in the United States, the joke would be on me, I cannot say. Then I have the recollection that some time ago I made a speech at a learned Society, whose name at the moment I cannot recollect; I know Sir Ernest Rutherford was there as the guest of the evening, and somehow or other, I cannot discover how, I gave the deepest offence, because one of the subsequent speakers pointed out, in terms of strong complaint, that in the presence of Sir Ernest Rutherford I had no right to speak about atoms in the light-hearted way I did.

You will therefore see what a very restricted field I have before

me, and I am still waiting for that friendly lead to enable me to resume my seat, before I am at last compelled to say something about the subject of the toast. I have had no scientific training whatsoever, having parted from mathematics at fifteen, never to resume the most distant acquaintance with them, knowing nothing of chemistry except by way of making smells at school in a cellar by the river Esk, which Professor Baker knows as well as I do, and I have to confess that I have followed a calling in which absolute knowledge and abstract science are not merely at a discount, but not understood at all. I have therefore always conceived a great admiration—I do not say for abstract science, but for those sciences in which pure knowledge is the real goal of men and women of pure science. You see, among lawyers there is no such thing as the desire to know the law in the abstract. You read law in order to get briefs and in order to win cases (sometimes it does equally well to lose them), and to obtain that promotion which comes with good luck and sound digestion, but as to a burning flame of desire to know what the law on any and every subject is, we know nothing of it.

I have always understood that, when you come to a man of pure science, he has no particular desire to advance human prosperity and to add to human happiness. Those things do come. Sometimes by accident he invents a gas, which prevents your feeling the pain of having your teeth pulled out; but his objective, his real goal, is to know, and to know more and more, and that is the charm of research. I was always told that your pride was to investigate something which you did not know and which led you nowhere, and left you no wiser at the end than at the beginning. This was the kind of thing I was trying to say on the other occasion. It has always seemed to me a very high and noble thing, much too high and noble for me. As far as I have been able to make out, pure scientific research now is largely connected with things you cannot possibly get at and can only know about by finding out what they do—sometimes very inconvenient things. I am told that no one has ever known what electricity is, except the undergraduate who said that he had known but had forgotten, but you find out curious effects in the way of making things twirl round and round, which the scientist has to use mysterious terms to explain. To take another example. We used to hear a lot about vitamins—things that are only postulated, because when you come down to the bare bones of the subject, if you eat one thing you thrive and if you eat another thing you do not, and I believe that is at the bottom of the present theory of the things you carry about in untold millions in your veins, which eat one another up and thereby preserve you

from immediate dissolution. You are perpetually finding yourselves on the verge not only of the unknown, but also of the unknowable, where you must postulate something you cannot possibly know, because there is no other explanation of the things you do dimly perceive. Hence you must invent something that cannot possibly be known at all.

In the course of the next four speeches, which may not have been entirely prepared beforehand, I expect to hear a word or two showing conclusively that abstract science is not really this at all, nor is this what it really means. All I can hope is that the Chemical Society will continue to pursue abstract science, to tread the noble path of knowledge for its own sake, to find (incidentally) advantages such as ought to attend on those who are entirely disinterested, and to flourish like a green bay tree. I give you the Toast of the Chemical Society, and ask your leave to couple with it the name of your President.

The PRESIDENT in reply, thanked Viscount Sumner for the kind way in which he had proposed the Toast. He welcomed among the guests present, not only Viscount Sumner, but especially Prof. Matignon, the representative of the French Chemical Society, and Prof. Schlenk, the President of the German Chemical Society, and stated that but for an attack of influenza, Prince Ginori Conti, the President of the Italian Chemical Society, would also have been with us. Their readiness to join in the Annual Meeting of the Chemical Society showed that not only in politics, but also in Science, the spirit of Locarno had begun to prevail. The President then referred to the loss sustained by the Society of the oldest and the youngest of its Past Presidents, Sir William Tilden and Dr. Crossley, and concluded his speech by pointing out the danger of publishing insufficiently considered hypotheses.

In proposing the Toast of "The Guests," Sir WILLIAM J. POPE stated that among the Guests present were not only men distinguished in Chemistry and in other branches of science, but also eminent men not associated with science. Though experiencing difficulty in making his selection, he coupled with the Toast the names of Sir E. Rutherford, President of the Royal Society, Professor Camille Matignon, representing the French Chemical Society, and Hofrat Professor Dr. W. Schlenk, President of the German Chemical Society.

In responding, Sir ERNEST RUTHERFORD said :—

Mr. President, my Lord, Ladies, and Gentlemen, it is a very great pleasure for me to be present here this evening, for I feel that I am among friends, and it is also a very great pleasure for me to reply, I am afraid very inadequately, to the toast of your Guests. I

am sure we are all very grateful for your hospitality and we appreciate the good company we have had this evening. I must also express my personal thanks to my colleague, Sir William Pope, for the kind way he has spoken of me. I do not remember any previous occasion when Pope and I have spoken on the same subject when sparks did not fly, but this evening must be an exception. In the very complimentary remarks about me and my work, I noted a certain sub-acidness which is characteristic of my friend. In this connexion, I am reminded of the stories which I used to read when I was in Canada, some twenty years ago, of the conversations between Mr. Dooley and Mr. Henessey, and there is one which I think is somewhat appropriate this evening. Mr. Henessey and Mr. Dooley were discussing the little troubles that have arisen from time to time between America and ourselves, and after an amusing dialogue, Dooley ended up the conversation in this way. He said, " After all, what can one expect from members of the same family with the same common language of abuse ! "

I have been acclaimed as a chemist this evening, and I feel very proud of the fact, but I know the regard in which I am held by my chemical friends is due to the fact that I am entirely ignorant of chemistry, and they all know it. During my life, however, I have made several minor incursions into the pure chemical arena, and it may be of interest if I briefly recall them, since I take a certain pride in my temerity.

Some of you may remember that many years ago Professor Boltwood of Yale University made the discovery that a preparation of actinium, carefully purified, grew radium at a rapid rate. This was a very important experiment, since it indicated that actinium was the long-looked-for radioactive parent of radium. I happened to have an actinium preparation in my laboratory, and after certain chemical treatment I obtained two fractions, both of which showed the characteristic radiating properties of actinium. One of these fractions grew radium at a rapid rate, whilst the other—a much more active preparation—did not grow radium at all. It was thus clear that actinium could not be the parent of radium, and Professor Boltwood was able to show later that the substance which he had supposed to be actinium, from the chemical properties assigned to it, was not actinium at all, but a new element which he named ionium. My friend Boltwood informed me, and I am sure quite rightly, that my luck in separating the two fractions was purely accidental, and due to the inadequacy of the chemical treatment which I had used.

The other incursion I made was some twenty years ago. I was asked by the late Sir William Ramsay to come to a meeting of the

Chemical Society in Burlington House to hear a paper by him on the volume of the radium emanation, that is, the volume of this gas when in equilibrium with one gram of radium. In an interesting lecture, he concluded that this volume was about ten cubic millimetres. Now, like Professor Baker, I make theories and sometimes stick to them. From certain calculations, I had estimated that the volume of the emanation must be about one cubic millimetre, so I intimated to the lecturer that I was fairly sure that 90 per cent. of the gas he had measured must be due to impurities. He naturally retorted that he was dealing with facts and that the theories must be altered to fit them. As a result of special experiments on the purification of the emanation, I was able to show, years later, that this first estimate of Ramsay was of the wrong order of magnitude. I have had such good luck in these chemical incursions that I do not propose to venture again.

Sir William Pope has told you that in a century's time I or my successor will not be a Professor of Physics, but professor of an evanescent science to be swallowed up by the advance of chemistry. I look at it from a rather different angle, and you can make what deduction you care to from the fact that I have a laboratory alongside Professor Pope, who has allowed me to occupy a part of his. We are also very sensible of the great work this Society has done for Chemistry since its foundation. There has been, as Sir William Pope has said, a very close relation between physics and chemistry during the last twenty years, and I hope that this may long be continued, and that in our individual directions we may continue to react with one another, but I hope with not too much heat. Although many advances have been made, we physicists recognise, probably even more than chemists, how relatively little we have accomplished and how much there is to be done before we can really tackle the great problem of chemical combination, which is, after all, the main *raison d'être* of this great Society.

While our knowledge of atomic structure has grown rapidly in recent years, it is still far from completion. It is at present going through a great change, due to the application of a new or wave mechanics to atomic problems. This new method has proved very powerful and fruitful in attacking certain types of problems, but has the disadvantage that it does not specify the position or motions of the electrons which make up the structure of the outer atom. The whole subject is at the moment in a transition stage, but we may hope to see a considerable clarification during the next four years. I hope there will also emerge new methods for attacking the fundamental problem of chemistry, namely, the way in which two or more elements combine.

A number of attacks have already been made on this question, some by men I see around me, but we cannot but recognise that it is a problem of great difficulty and complexity. We know little in detail of the magnitude and nature of the forces which bind atoms together, but I have sometimes thought that the natural way would first be to study the combination of atoms of matter of the same kind in the crystalline form, for example in metals. If an explanation can be found for the simplest combinations, it may lead to an attack of the more complex problem of combination of atoms of different kinds. Everyone must recognise the importance of this problem, for, after all, we ourselves and the world about us are examples of such chemical combinations, but fundamentally we know little, and have much to learn. I am hopeful that ultimately the physicist may be able to throw light on this greatest of problems which lies at the basis of chemistry.

Before concluding, I would like to refer to the great work initiated by your President by that study of matter in pure form, or rather in the dry form, which has shown such peculiar properties and reactions, or rather absence of reactions. It always seems to me that these results indicate that our present theories of chemical combination are at best very superficial, and I wish him every success in this important field of work.

Now I must not take more of your time, as we have our foreign guests to respond to this toast, but on behalf of all our non-chemical brethren and non-speakers, I must express our thanks for a very enjoyable evening, and our thanks to Sir William Pope for the very kind way he has proposed the toast of the guests.

Professor Camille Matignon said :—

Le Président de la Société Chimique de France, M. le Prof. Urbain, empêché n'a pu répondre à votre aimable invitation, et il m'a chargé de l'excuser et de vous exprimer en même temps tous ses regrets de ne pas être ce soir parmi vous.

J'ai accepté bien volontiers de le remplacer.

Si vous perdez beaucoup à cet échange, par contre, je m'en réjouis profondément, puisque cette substitution me procure l'agréable mission d'être l'interprète de mes compatriotes auprès de la Chemical Society, et de vous apporter l'expression de la très cordiale confraternité des chimistes français. C'est pour moi, délégué officiel pour la première fois en Grande Bretagne, un honneur dont je suis très fier.

Je suis heureux de vous donner l'assurance que la tension des liens qui nous unit à vous ne s'est pas relâchée et de vous confirmer l'inébranlable persistance de nos affections individuelles et de nos attachements collectifs.

Et comment, Messieurs, pourrait-il ne pas en être ainsi ? Sans

faire état des sentiments d'estime et d'attachement coutumiers entre nos deux pays, peut-il être cimenté, entre citoyens de nations différentes, une union plus intime que celle qui nait de la coopération intellectuelle ?

Ouvriers d'une même œuvre ; collaborateurs associés, en vertu d'une entente tacite, pour la recherche de la solution des mêmes problèmes ; travailleurs guidés par une même passion, la plus noble et la plus saine, celle de la recherche de la vérité et des applications de cette vérité à l'amélioration continue des conditions matérielles de l'humanité. Comment pourrions-nous résister à l'attraction, génératrice de chaudes sympathies, qui nous attire les uns vers les autres sur ce terrain d'union sacrée ?

Permettez-moi, Messieurs, puisque j'en ai l'occasion, de vous dire toute mon admiration pour la science anglaise. Cette admiration ne date pas d'hier. Elle a pris naissance au moment où, assis sur les bancs de l'Université, je pénétrais dans ce monument de la Science, en perpétuel état d'évolution et de développement, bâti avec les faits accumulés et coordonnés par nos devanciers. C'est alors que l'œuvre d'un de vos savants, Sir William Thompson, depuis Lord Kelvin, frappa profondément ma jeune imagination. Habile expérimentateur, algébriste et géomètre consommé, ingénieux, audacieux, doué d'un rare esprit d'invention, Lord Kelvin a embrassé par l'étendue de ses conceptions, à la fois le domaine entier de la théorie et celui des applications pratiques ; il est resté pour moi depuis cette époque, le type accompli du génie britannique.

Ce qui m'avait frappé chez Lord Kelvin et que j'ai retrouvé depuis chez la plupart de vous tous, c'est une puissante faculté imaginative, qu'on ne rencontre au même degré chez aucun peuple d'Europe, et qui vous permet de vous représenter un ensemble très compliqué de choses concrètes, de les voir chacune à sa place, en quelque sorte avec son mouvement et sa vie. Une autre caractéristique de la science anglaise, qui se dégageait nettement de l'œuvre de Lord Kelvin, c'est cette audace, à laquelle faisait allusion M. le Prof. Moureu, dans une de vos précédentes réunions annuelles ; tandis qu'en général, le chercheur français est prudent et souvent timoré, l'investigateur anglais semble, au contraire, rechercher dans le domaine de la science, tout ce qui est imprévu, tout ce qui est audacieux. Les résultats si curieux et si suggestifs obtenus par votre Président M. le Prof. Baker dans les travaux qu'il nous a exposé cet après-midi, travaux qui constituent à la fois un modèle d'expérimentation mais aussi un bel exemple d'audace, ne nous en apportent-ils pas une nouvelle vérification ?

Extraordinaire puissance de la faculté d'imaginer des choses

concrètes; audace dans la conception; audace dans l'expérimentation; ces éminentes qualités, qui sont à la base de l'esprit d'invention, caractérisent votre esprit scientifique. Elles ont été génératrices de vos découvertes les plus retentissantes.

Depuis mes débuts dans la science, mon enthousiasme pour la science anglaise n'a cessé de se consolider, et de se développer au fur et à mesure que se succédaient les innovations sensationnelles sorties de vos laboratoires. Ce fût d'abord la mise au jour par Lord Rayleigh et Ramsay d'un nouvel élément de l'air, l'argon, l'un des événements scientifiques les plus marquants de ma génération, puis vinrent l'hélium, le néon, le krypton, le xénon, qui se rangèrent avec une discipline parfaite dans une nouvelle colonne de la classification de Mendeléeff.

Avec ces nouveaux gaz d'une inertie chimique absolue, c'était un domaine entièrement nouveau acquis à la science; mais la classification de Mendeléeff, rajeunie par ces nouvelles découvertes, devait prendre plus tard son plein essor et atteindre son complet développement avec la loi de Moseley. Elle a pris désormais, grâce à vous, Messieurs, une place si importante dans la science, qu'elle domine à l'heure actuelle toute la chimie et condense en elle toutes nos connaissances sur la matière.

Enfin, Messieurs, car je suis obligé d'abréger, c'est d'un laboratoire de l'Université de Cambridge qu'est sortie toute l'atomistique moderne. Par l'étude systématique des phénomènes, alors si complexes et si déconcertants, de la conductibilité électrique des gaz, phénomènes dans lesquels on faisait jouer aux poussières un rôle souvent important, J. J. Thomson a dégagé avec netteté la notion d'ion gazeux, précisé celle de l'électron, et établi des méthodes cinétiques électriques d'une délicatesse, d'une subtilité qui dépassent toutes les prévisions les plus optimistes. Grâce à ces méthodes, il est possible d'agir avec sûreté et précision sur les atomes et les molécules, c'est à dire sur des individualités dont l'extrême petitesse n'a plus pour nous aucun sens réel; ces superinfiniment petits, que nous ne pourrons probablement jamais voir, on les pèse, on les classe, on les sépare, dès qu'ils présentent la moindre différence dans leurs masses et on les dénombre en mettant en évidence leur présence individuelle par certaines de leurs manifestations accessibles à nos sens.

La découverte des corps radioactifs, l'étude rapide de leurs propriétés résultent de la mise en œuvre de ces mêmes méthodes.

Quel chemin parcouru, Messieurs, depuis le jour où le premier ministre d'Angleterre, le Marquis de Salisbury, présidant à Oxford en 1894 à la British Association, prononçait son discours retentissant sur "Les limites actuelles de notre science," après avoir exposé les

apports de Dalton, de Kirchoff, de Mendeléeff, à la notion de l'élément chimique, l'éminent homme d'état ajoutait : " Ces triomphes successifs ne nous ont pas beaucoup avancés vers la solution des problèmes que les atomes élémentaires ont présentés à l'humanité pendant des siècles. . . . Savoir ce qu'est la particule insécable, si c'est un mouvement, une chose, un tourbillon, un point ayant de l'inertie ; déterminer s'il y a une limite à la divisibilité de cet être, et s'il en est ainsi, deviner comment cette limite est imposée ; décider si la longue liste des éléments est définitive ou si quelques uns ont une commune origine, toutes ces questions restent environnées de ténèbres aussi profondes qu'autrefois. Le rêve qui soutenait les alchimistes dans leurs pénibles travaux n'a sûrement point été réalisé mais il n'a point encore été dissipé. De ce côté, les frontières de notre science restent ce qu'elles étaient il y a un grand nombre de siècles."

Si ces conclusions négatives du Marquis de Salisbury sont désormais périmées, c'est à l'École Anglaise que nous le devons, c'est elle qui a été l'initiatrice des progrès merveilleux réalisés dans le domaine de l'atomistique, et c'est elle qui a apporté une part des plus importantes à son développement.

Messieurs, Je remercie bien vivement encore M. le Professeur Baker et les membres du Conseil de la Chemical Society pour leur invitation à cette brillante fête de la science. Je lève mon verre en l'honneur de la Science Britannique et de ses futurs succès, je bois à la prospérité de la Chemical Society, à la vieille et durable amitié qui unit la Chemical Society et la Société Chimique de France et puisque je suis Vice-président de la Société de Chimie Industrielle, permettez-moi de l'associer également à cette union.

Hofrat Professor Dr. W. SCHLENK said :—

Mr. President, Ladies, and Gentlemen, I desire to express my thanks to you for your kind invitation to me to be your guest. When I got your invitation my pleasure was a double one. I was glad of the opportunity to spend some hours in your company and rejoiced by the thought that this invitation was a sign of the improvement in international relations. I think, ladies and gentlemen, that every chemist must take a great interest in good international relations, because scientific work is international, and I am sure there is indeed nothing which could be an obstacle towards a good international relationship; certainly, ladies and gentlemen, there is nothing so important as a happy international relationship. In time of need we feel like children of our country, so British chemists feel as Britons, and other chemists as children of their country. This is natural, but an idealism is necessary for the restoration of the happy relationship we had before. Your invit-

ation gives me the hope that we are on the right road to regain what formerly was a matter of course, namely a mutual respect and confidence. With these remarks, ladies and gentlemen, accept my best thanks for your invitation, and my good wishes for your Society.

Ordinary Scientific Meeting, Thursday, April 7th, 1927, at 8 p.m., Professor H. Brereton Baker, C.B.E., LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death on March 8th, of Mr. John Henry Smith, who was elected a Fellow on December 7th, 1911, and announced that:

1. The following Committees for 1927–1928 had been appointed by the Council:

Finance Committee: J. L. Baker, F. P. Dunn, Charles A. Hill, G. T. Moody, J. C. Philip, R. H. Pickard, W. P. Wynne, and the Officers (Treasurer as Chairman), with the Assistant Secretary as Secretary.

House Committee: J. L. Baker, H. B. Dixon, Sir Herbert Jackson, Sir Robert Robertson, Alexander Scott, J. M. Thomson, and the Officers, with the Assistant Secretary as Secretary.

Library Committee: T. A. Henry, J. R. Partington (Chairman), Alexander Scott, N. V. Sidgwick, S. W. Smith, J. F. Spencer, the Officers, together with representatives of contributing Societies, with the Librarian as Secretary.

Publication Committee: M. P. Applebey, H. Bassett, H. V. A. Briscoe, H. W. Dudley, U. R. Evans, J. J. Fox, R. Whytlaw Gray, A. J. Greenaway, T. A. Henry, C. K. Ingold, J. Kenyon, H. King, H. McCombie, T. S. Moore, G. T. Morgan, K. J. P. Orton, J. R. Partington, J. C. Philip, F. L. Pyman, E. K. Rideal, R. Robinson, N. V. Sidgwick (Chairman), and the Officers, with the Editor as Secretary.

Research Fund Committee: A. J. Allmand, E. C. C. Baly, F. E. Francis, W. N. Haworth, C. K. Ingold, W. H. Mills, F. L. Pyman, Sir Robert Robertson, N. V. Sidgwick, Sir James Walker, and the Officers, with the Assistant Secretary as Secretary.

2. The following letter of thanks had been received from Professor W. Schlenk, President of the German Chemical Society:

Berlin N. 4, den 29 März, 1927.
Hessische Str. 1.

Herrn Professor Baker,
Präsident der Chemical Society.

Hochverehrter Kollege,

Nach meiner Rückkehr aus London ist es mir ein herzliches Bedürfnis, Ihnen und Ihrer Gesellschaft nochmals herzlich zu danken für die genossene

Gastfreundschaft und für das so freundliche Entgegenkommen, dessen ich mich erfreuen durfte. Die freundliche Aufnahme, welche ich im Kreise der Chemical Society gefunden habe, lässt mich hoffen, dass die historischen guten Beziehungen zwischen englischen und deutschen Chemikern sich gewiss wieder einstellen werden, eine Tatsache, welche meinen hiesigen Freunden ebenso zur Freude gereicht wie mir selbst.

Nehmen Sie nochmals den besten Dank entgegen,
Ihres sehr ergebenen,
W. SCHLENK.

3. The Council had accepted the offer contained in the following letter from the Mond Nickel Company, Limited, and that copies of the full-sized and of the reduced-size chart could be obtained by Fellows on application to Mr. S. E. Carr :

VICTORIA STATION HOUSE,
VICTORIA STREET,
LONDON, S.W. 1.
31*st March*, 1927.

THE SECRETARY,
THE CHEMICAL SOCIETY,
BURLINGTON HOUSE,
W. 1.

Mond Process Chart.

DEAR SIR,

In view of numerous applications received by us from time to time for particulars of our method of refining nickel from Canadian ore by the Mond Carbonyl Process, a Chart, of which the enclosed is a reduced-size facsimile, has recently been prepared.

Should the full-sized chart, which measures 48″ (122 c/m) × 36″ (91 c/m), be of service to you and/or any of your members, we shall be pleased, upon hearing from you, to forward, without charge, one or more charts, together with such additional copies of the enclosed reduced sized facsimile as you may indicate.

Yours faithfully,
For The Mond Nickel Company, Limited,
F. B. HOWARD WHITE.
Secretary, Research and Development Dept.

The following were formally admitted Fellows of the Chemical Society: W. H. Brindley, Stanley E. Pusey, and Thomas K. Walker.

Certificates were read for the first time in favour of :

William John Bissell, 863, London Road, Westcliff-on-Sea.
Leslie George Scott Brooker, Ph.D., B.Sc., A.I.C., 54, Augustine Street, Rochester, N.J., U.S.A.
Victor Scotthorn George, 139, Bearwood Road, Smethwick.
William Claude Lyle, B.Sc., A.I.C., 308, Dumbarton Road, Glasgow.
Cecil Arthur Poulson, Haverstock, Shawlands, Glasgow.
John Storrow Rumbold, B.Sc., A.I.C., 22, Calton Avenue, Wavertree, Liverpool.

The following certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2):

Genshiro Kurabayashi, The Tokyo Higher Normal College, Koishikawaku, Tokyo.

Dr. J. G. F. Druce and Dr. H. Phillips were appointed Scrutators, and a ballot for the election of Professor Richard Willstätter as an Honorary Fellow was held. Professor Willstätter was subsequently declared duly elected.

The following papers were read:

"Trypanocidal action and chemical constitution. Part VI. Amphoteric *s*-carbamidoarylarsinic acids." By H. KING.

"On active nitrogen. Part III. Active nitrogen and the metals." By E. J. B. WILLEY.

"Esterification in mixed solvents." By B. V. BHIDE and H. E. WATSON.

"The alkaloids of ipecacuanha. Part IV." By W. H. BRINDLEY and F. L. PYMAN.

FARADAY LECTURE.

An Extra Meeting of the Society will be held in the Theatre of the Royal Institution, Albemarle Street, W. 1. (by the courtesy of the Managers), on Wednesday, May 18th, 1927, at 5.30 p.m., when the Faraday Lecture, entitled "Problems and Methods in Enzyme Research," will be delivered by Professor Dr. Richard Willstätter.

Admission will be by ticket only. Each Fellow of the Society is entitled to two tickets, application for which should be made as early as possible to the "Assistant Secretary, Chemical Society, Burlington House, W. 1."

RESEARCH FUND COMMITTEE.

A meeting of the Research Fund Committee will be held in June next. Application for Grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W. 1, must be received on or before Wednesday, June 1st, 1927.

All persons who received grants in June, 1926, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned by June 1st.

List of Papers, or Abstracts thereof, received between March 17th and April 7th, 1927. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The action of caustic alkalis on the 3-halogeno-4-nitrosodimethylanilines." By H. H. HODGSON and J. S. WIGNALL.

"Metallic hydroxy-acid complexes. Part IV. Complexes formed by copper with the monohydroxy monobasic acids." By I. W. WARK.

"Co-ordination compounds of beryllium and *m*- and *p*-nitrobenzoylacetone." By H. BURGESS.

"The crystal structure of quinol. Part II." By W. A. CASPARI.

"The scission of diaryl ethers and related compounds by means of piperidine. Part I. The scope of the method and its use in determining the constitution of some nitro-derivatives." By R. J. W. LE FÈVRE, S. L. M. SAUNDERS, and E. E. TURNER.

"The system $Ca_2Fe(CN)_6$–$Na_4Fe(CN)_6$–H_2O. Part II." By M. FARROW.

'The effect of mercury salts in the nitration of aromatic systems." By P. V. MCKIE.

"The structure of normal fructose: crystalline tetramethyl β-methylfructoside and crystalline tetramethyl fructose (1 : 3 : 4 : 5)." By W. N. HAWORTH, E. L. HIRST, and A. LEARNER.

"The reaction between manganese salts and sodium hypochlorite in the presence of certain other salts." By B. E. DIXON and J. L. WHITE.

"Reduction products of the hydroxyanthraquinones. Part VIII." By E. J. CROSS and A. G. PERKIN.

"Reduction products of the hydroxyanthraquinones. Part IX." By A. MACMASTER and A. G. PERKIN.

"Low-temperature oxidation of hydrocarbons." By J. S. LEWIS.

"The action of halogen-substituted phenylhydrazines upon dihydroxytartaric acid." By F. D. CHATTAWAY and W. G. HUMPHREY.

"A study of the chemiluminescence of phosphorus vapour." By E. J. BOWEN and E. G. PELLS.

"The synthesis of *meso*-alkyl and *meso*-aryl anthracene derivatives. Part II." By E. DE B. BARNETT, J. W. COOK, and J. L. WILTSHIRE.

"The use of titanous chloride in the volumetric estimation of copper and iron." By W. G. EMMETT.

"The effect of hydrochloric acid on the electrode potential between mercury and mercurous chloride. By S. R. CARTER, F. M. LEA, and R. ROBINSON.

"The oxidation-reduction potentials of mercurous and mercuric chlorides in hydrochloric acid solution." By S. R. CARTER and R. ROBINSON.

"The system ferric oxide–arsenic acid–water at low concentrations of arsenic acid." By N. H. HARTSHORNE.

"A process for the dehydration of alcohol." By E. L. SMITH.

"A method for the estimation of small quantities of water in alcohol." By E. L. SMITH.

"Researches in the menthone series. Part IV. *iso*Menthols and *iso*menthones." By J. READ, G. J. ROBERTSON, and M. R. COOK.

"Humic acid in British coals." By F. W. SMITH and D. H. JAPES.

"Studies of valency. Part VIII. The molecular structure of Vernon's dimethyltelluronium salts." By T. M. LOWRY and R. R. GOLDSTEIN.

"The action of nitrous acid on substituted *p*-phenylenediamines. Part I. Benzyl-*n*-butyl-*p*-phenylenediamine." By J. REILLY and P. J. DRUMM.

"The system lead chloride–lead iodide–water." By A. L. M. SOWERBY.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

(a) *From Dr. Otto Rosenheim.*

DEAN, JOHN. The organic compounds of tellurium and selenium belonging to the alcohol series. Goettingen 1855. pp. vi + 51.

LEWENAU, JOHANN EDLEN VON. Chemische Abhandlung über das Selen. Wien 1823. pp. viii + 144 + 3 tables.

LITTLE, GEORGE. On selenium and some of the seleniurets. Göttingen 1859. pp. 40.

OPPENHEIM, ALPHONS. Beobachtungen ueber das Tellur und einige seiner Verbindungen. Goettingen 1857. pp. 36.

RATHKE, BERNHARD. Beiträge zur Kenntniss des Selens. Halle 1869. pp. ii + 58. ill.

STOLTE, HENRICH. Ueber organische Selenverbindungen. Berlin 1887. pp. 48.

(b) *Miscellaneous.*

ACADÉMIE DES SCIENCES DE L'UNION DES RÉPUBLIQUES SOVIÉTIQUES SOCIALISTES. Travaux sur le radium et les minerais radioactifs. 2 vols. Leningrad 1924—1926. pp. viii + 176, vi + 276. ill. [In Russian.] (*Recd.* 15/3/27.) From the Academy.

AMERICAN ELECTROCHEMICAL SOCIETY. Transactions. Vol. I, etc. Philadelphia 1902 +. (*For circulation.*)

—— —— General indexes. Vols. I—XX, 1902—1911, Vols. XXI—XL, 1912—1921. South Bethlehem 1913, and New York 1927. (*Reference.*) From the Faraday Society.

ARMSTRONG, HENRY EDWARD. Essays on the art and principles of chemistry, including the first Messel memorial lecture. London 1927. pp. xxxii + 276. ill. 15*s.* net. (*Recd.* 7/4/27.) From the Publishers: Messrs. Ernest Benn.

CHIMIE INDUSTRIELLE d'après les travaux les plus récents. Par un professeur de chimie. 2 vols. [n.d.] pp. 274 + 43 plates. (*Reference.*) From Mr. S. H. Woolhouse.

DON, JOHN. The filtration and purification of water for public supply. (Excerpt Minutes of Proceedings of the Meetings of the Institution of Mechanical Engineers, 1909.) pp. 210. ill. From the Author.

DON, JOHN, and CHISHOLM, JOHN. Modern methods of water purification. 2nd edition. London 1913. pp. xviii + 398. ill. (Second copy.) From Mr. John Don.

DYER, Calico Printer, Bleacher, and Finisher. Vol. LVII, etc. London 1927 +. (*Reference.*) From the Society of Dyers and Colourists.

ERNÄHRUNG DER PFLANZE. Illustrierte Halbmonatsschrift über Fortschritte im Ackerbau und landwirtschaftlichen Düngewesen des In- und Auslandes. Year XXIII, etc. Berlin 1927 +. (*Reference.*) From the Deutsche Kalisyndikat.

HADFIELD, SIR ROBERT ABBOTT. Metallurgy and its influence on modern progress, with a survey of education and research. London 1925. pp. xvi + 388. ill. 25*s.* net. (*Recd.* 18/3/27.) From the Author.

INSTITUTE OF METALS. Journal. Vol. I, etc. London 1909 +. (*For circulation.*)

—— —— Name-Subject index to vols. I—XXV, 1909—1921. London 1922. (*For circulation.*) From the Faraday Society.

JAPAN. *Imperial Academy.* Proceedings. Vol. II, etc. Tokyo 1926 +. (*Reference.*) From the Academy.

NATIONAL BENZOLE ASSOCIATION and UNIVERSITY OF LEEDS. *Joint Benzole Research Committee.* Fourth report. London 1927. pp. 248. ill. (*Recd.* 2/4/27.) From Mr. W. H. Coleman.

RUSSELL, SIR EDWARD JOHN. Soil conditions and plant growth. 5th edition. London 1927. pp. viii + 516. ill. 18*s.* net. (*Recd.* 22/3/27.) From the Author.

TEXTILE RECORDER. Vol. XLIV, etc. Manchester 1927 +. (*Reference.*) From the Society of Dyers and Colourists.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. VI. Part iii. Berlin 1927. pp. 481—720. *M.* 10. (*Recd.* 29/3/27.)
From the Publishers : Herren Urban & Schwarzenburg.

II. *By Purchase.*

ALCHEMISTISCHE BLÄTTER. Erste deutsches Fachblatt für alle Gebiete der Alchemie. Year I, etc. Berlin 1927 +. (*Reference.*)

BAARS, E. Über den Zustand des Ammoniaks in wässriger Lösung. (Sammlung, Vol. XXIX.) Stuttgart 1927.

BARRY, THOMAS HEDLEY, DRUMMOND, ALAN ASHBY, and MORRELL, ROBERT SELBY. The chemistry of the natural and synthetic resins. London 1926. pp. x + 196. 21*s.* net. (*Recd.* 21/3/27.)

HEVESY, GEORG VON. Das Element Hafnium. Berlin 1927. pp. iv + 49. ill. *M.* 3.60. (*Recd.* 29/3/27.)

JENNINGS, ARTHUR SEYMOUR. Paint and colour mixing : a practical handbook. 7th edition. London 1926. pp. 341. ill. 12*s.* 6*d.* net. (*Recd.* 17/3/27.)

KELLNER, OSKAR. The scientific feeding of animals. Authorised translation by WILLIAM GOODWIN. [2nd edition.] London 1926. pp. xiv + 328. 8*s.* 6*d.* net. (*Recd.* 29/3/27.)

LEGENDRE, R. La concentration en ions hydrogène de l'eau de mer. Le pH ; méthodes de mesure ; importance océanographique, géologique, biologique. Paris 1925. pp. viii + 292. ill. 30 *fr.* (*Recd.* 22/3/27.)

LIPPMANN, EDMUND OSKAR VON. Studien zur Geschichte der Chemie : Festgabe zum siebzigsten Geburtstage. Edited by JULIUS RUSKA. Berlin 1927. pp. vi + 242. *M.* 19.50. (*Recd.* 29/3/27.)

MARGOSCHES, BENJAMIN MAX, with the collaboration of LUDWIG FRIEDMANN and LISBETH HEERMANN-WOLF. Die Jodzahlschnellmethode und die Überjodzahl der Fette. Die Aktivierung des Jods durch Wasser. (Die chemische Analyse. Vol. XXV.) Stuttgart 1927. pp. x + 228. (*Reference.*) *M.* 16.20.

RUSKA, JULIUS. Tabula Smaragdina : ein Beitrag zur Geschichte der hermetischen Literatur. Heidelberg 1926. pp. vii + 248. *M.* 32. (*Recd.* 23/3/27.)

SUTERMEISTER, EDWIN. Casein and its industrial applications. New York 1927. pp. 296. ill. 21*s.* net. (*Recd.* 29/3/27.)

WAIT, DOUGLAS. The manufacture of enamel paints : a practical handbook. London 1927. pp. viii + 153. ill. 10*s.* 6*d.* net. (*Recd.* 17/3/27.)

WAR OFFICE. Manual of the medical aspects of chemical warfare. London 1926. pp. 92. ill. 9*d.* net. (*Recd.* 17/3/27.)

III. *Pamphlets.*

AERONAUTICAL RESEARCH COMMITTEE. Reports and Memoranda. No. 1016. Some physico-chemical studies on the effect of sunlight on cotton. By GUY BARR and ISABEL HODGSON HADFIELD. London 1926. pp. 22. ill.

MINES DEPARTMENT. *Safety in Mines Research Board.* Paper No. 31. Laboratory methods of determining the inflammability of coal dusts : historical survey and preliminary examination of the problems involved. By A. L. GODBERT. London 1927. pp. 68. ill.

—— —— Paper No. 32. The study of flame movement. By OLIVER COLIGNY DE CHAMPFLEUR ELLIS. London 1926. pp. 35. ill.

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Fuel Research.* Physical and chemical survey of the national coal resources, No. 7. Methods of analysis of coal. London 1927. pp. vi + 35. ill.

—— —— Physical and chemical survey of the national coal resources, No. 8. An investigation of the caking power of coal. By JOHN THOMAS BURDEKIN. London 1927. pp. iv + 21. ill.

—— —— Technical Paper No. 15. Carbonisation of coal in continuous vertical retorts. "Holmside" (Durham) coal with experiments on the production of coal gas of high calorific value. London 1926. pp. iv + 44. ill.

—— —— Technical Paper No. 17. Low temperature carbonisation. Vertical retorts at H.M. Fuel Research Station. By CECIL HOWARD LANDER and J. FRASER SHAW. London 1927. pp. 7. ill.

STOWELL, FLAXNEY PERCIVAL. Physical and chemical conditions in the sea-water of the Zoological Society's aquarium—a comparison with the water of the open sea. (From the *Proc. Zool. Soc.*, 1925.)

—— The purification of sea-water by storage. (From the *Proc. Zool. Soc.*, 1926.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, May 5th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death on March 28th, of Mr. Hildyard John Eglinton Dobson, who was elected a Fellow on May 3rd, 1923.

Certificates were read for the first time in favour of:

James Bell, jun., B.Sc., A.I.C., 3, Finnart Terrace, Greenock.
William Ryle Clifford Curjel, B.A., Netherside, Woodbridge, Suffolk.
Albert de Bussy Goodman, Hatchgate, Massetts Road, Horley, Surrey.
Bhaba Nath Das Gupta, B.Sc., M.B., Noakhali, Bengal, India.
Cecil Owen Harvey, B.Sc., A.R.C.S., A.I.C., Government Laboratory, Clement's Inn Passage, Strand, W.C. 2.
James Shankland Merry, 22, Norwood Grove, Liverpool.

Mr. F. H. Lowe and Dr. G. A. C. Gough were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Robert Andrew.
William Barklamb.
Fritz Alfred Bate, B.Sc.
Keith Lester Beak.
William Bradley, M.Sc.
Edwin Herbert Bunce, A.I.C.
David Henry Burton, B.Sc., A.R.C.S., A.I.C.
Charles McKenley Cameron.
Richard Chadwick, B.A.
Ronald Kington Christy, B.Sc.
Edgar Dawn Copley, B.A., B.Sc.
Thomas Eric Ellison.
Charles Forrester, F.I.C.
Gerald Charles Leake Griffin, B.A.
John Gurney, B.A.
James Charles Harral.
Norman Holt Hartshorne, M.Sc., A.I.C.
William Herbert Hatfield, D.Met.
Leonard Joseph Hooley, B.A., A.I.C.
George Robert Howard, B.Sc.
Thomas Alfred Jenkinson, B.Sc.
Louis Arnold Jordan, D.Sc., A.R.C.S. F.I.C.
Arthur William Knapp, B.Sc., F.I.C.,
Jason Louis Edward Lewkowitsch, A.R.C.S.
James Hutchison McGregor, A.I.C.
Tarak Nath Majumdar.
Ernest Matthews, M.Sc., A.R.C.S., D.I.C.
Herbert Joseph Millward.
Alfred William Mond, B.A.
John Hopkinson Parker.
Dorothy May Lyddon Rippon, B.A.
Otto Leslie Shaw.
Arthur Shortt, B.Sc.
John Tomlinson, B.Sc.Tech.
Allan George Tyler, B.Sc.
Albert Denny Usher, B.Sc.
Carl Roman Ward, B.A.
Charles Barnett Wingfield.
Robert Louis Wormell.

The following papers were read:

"The nature of the alternating effect in carbon chains. Part XVIII. Mechanism of exhaustive methylation and its relation to anomalous hydrolysis." By W. HANHART and C. K. INGOLD.

"The interrelationships of the sulphur acids." By H. BASSETT and R. G. DURRANT.

"The constitution of the disaccharides. Part XIV. Melibiose and its relationship to raffinose." By W. CHARLTON, W. N. HAWORTH, and W. J. HICKINBOTTOM.

Extra Meeting held in the Theatre of the Royal Institution (by kind permission of the Managers) on Wednesday, May 18th, 1927, at 5.30 p.m., the President, Professor H. BRERETON BAKER, C.B.E., LL.D., F.R.S., occupying the Chair.

The company present numbered about 600.

In introducing the lecturer, the PRESIDENT said that they had met to honour the immortal name of Faraday. These Faraday Lectures were in no sense Memorial Lectures; the name of Faraday needed no memorial, for so long as science endured, the name of Faraday would be honoured and revered. In these Lectures, delivered triennially, the Chemical Society had had the co-operation of the most celebrated chemists and other men of science from all over the world, and that day it was able to add to that distinguished list the name of Richard Willstätter. Faraday was a border-line chemist, for although his discovery of benzene would entitle him to be called an organic chemist, most of his work dealt with the border-line of physics and chemistry. Prof. Willstätter was also a border-line chemist; the frontier on which he had won his fame was the frontier which joined chemistry and botany.

The President then asked Prof. Willstätter to deliver his lecture entitled: "Problems and Methods in Enzyme Research."

At the conclusion of the Lecture, the President, in presenting the Faraday Medal to Professor Willstätter, expressed the hope that it would be a happy souvenir of this great occasion.

In proposing a vote of thanks to the lecturer, Prof. W. H. Perkin paid a tribute to Prof. Willstätter for his outstanding work not only in connection with biochemical problems, but also in the various sections of pure organic chemistry. It had been rather difficult for those who had little or no practical acquaintance with the enzymes to keep touch with and follow the large number of important investigations which had been carried out in the laboratories of Prof. Willstätter. Fortunately, however, the Professor had recently

published two summaries containing the main results of the work which he and his co-workers had done in this field. From those summaries it was easy to appreciate how very difficult the work must always have been, and, in particular, how disappointing it must have been to find that these elusive substances lost their activity and other characteristic properties, and were sometimes even destroyed altogether, as the solution was concentrated. But it was far more instructive even than a study of those summaries to have the pleasant experience of listening to the author of all this work explaining the main results which had been achieved, and giving some idea of the amount of work which remained to be done in the future. They were all very greatly obliged to Prof. Willstätter for having given his brilliant and stimulating Lecture.

Prof. J. F. Thorpe, in seconding the vote of thanks, referred to Prof. Willstätter as a great organic chemist—so great that he was placed on a pinnacle as high as that occupied by his countrymen, Baeyer and Fischer. Prof. Willstätter had carried out epoch-making researches in a great number of branches of organic chemistry, any one of which would have made the reputation of any lesser man. With a courage which all admired, and which very few could emulate, he had left the " flowery " paths of organic chemical research and had entered that wilderness which was the province of the biochemist. Great things had been accomplished by the biochemists. The materials they had made, and the reactions they had discovered, were wonderful, but we still knew nothing of the mechanism of biochemical reactions, and until we did, we should know nothing of the meaning of life. It was only from the standpoint of organic structure that we could hope to obtain any insight into the mechanism of biochemical action, and therefore, when Prof. Willstätter had abandoned those " easy " syntheses and had entered the more difficult field, organic chemists welcomed the fact. Prof. Willstätter was still a young man; he had many years of active research before him, and they all hoped that he would continue his classical researches, and that his future work would be attended with every success. Organic chemists felt that if Prof. Willstätter failed in the study of the structure of the enzymes, then no one else would succeed.

The vote of thanks was accorded with enthusiasm, and, in making acknowledgment, Prof. Willstätter said :

" At this moment it is difficult for me adequately to express my feelings. Your invitation to give this Lecture and your award of this beautiful medal means for me the greatest distinction that could ever be conferred upon me, and the impressions of this hour are still further deepened by the more than warm and

friendly welcome you have given me, and which will ever live in my memory. Allow me to express my sincerest and most cordial thanks. By my reception into the circle of the Faraday Lecturers, you wish to associate me with that small band of scientists immortalised by your Society. I cannot but be aware of the distance that separates me from my great predecessors, but do I not owe this honour to your intention to unite together the scientists of every country and to let them share in paying homage to Faraday, who has so enriched all the world?

"In the last few days I have been privileged to visit Westminster Abbey and your museums and libraries. The impressions of these great works are vivid in my mind, for there are found the painter's brush, the sculptor's chisel, the poet's lyre, and thereto belongs also the scientist's ink, which the Koran even parallels with the martyr's blood. These lasting achievements of human spirit are international, they are the common possession of all mankind."

In concluding the business, the PRESIDENT expressed the Society's warm and appreciative thanks to the Managers of the Royal Institution for granting permission to hold this important celebration in this historic room. No one could stand in that room, with its associations of Davy, Faraday, and other great men of science, without profound emotion, and he was convinced of the fact that the Lecture being delivered there had helped to inspire Prof. Willstätter. The vote of thanks was accorded with acclamation:

Ordinary Scientific Meeting, Thursday, May 19th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT announced that Miss Gladstone had presented an album containing photographs of eminent Chemists and other Men of Science belonging to the late Dr. John Hall Gladstone, Past-President.

Professor Dr. Richard Willstätter was formally admitted an Honorary Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

Otto Guido Backeberg, B.A., M.Sc., A.I.C., University of the Witwatersrand, Johannesburg.

Leonard Bayley, 31, The Crescent, Friern Barnet, N. 11.

William Bleloch, B.Sc., Hazleyshaw, Albemarle Street, Kensington, Johannesburg.

Donald William Parker Boyd, M.A., c/o Messrs. Boileau & Boyd, Ltd., 91–93, Bride Street, Dublin.

Francisco Miguel Camps-Campins, B.Sc., 67, Frederick Road, Port-of-Spain, Trinidad.

Frederick Arthur Filby, B.Sc., 378, High Street North, East Ham, E. 12.
Robert Edwin Goldsbrough, Woodside, Great Horkesley, Colchester.
Vaidyanatha Subrahmanyan, B.A., Indian Institute of Science, Bangalore, India.

The following certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2):

Eugenie Sachs, 280, Market Street, Pretoria, S. Africa.

The following paper was read:

"New developments in the study of acid catalysis. The catalytic catenary." By H. M. DAWSON.

At the next Ordinary Scientific Meeting, to be held on June 2nd, the following papers will be read:

"The passivity of metals. Part I. The isolation of the protective film." By U. R. EVANS.

"Studies of valency. Part VIII. The molecular structure of Vernon's dimethyltelluronium salts." By T. M. LOWRY and R. R. GOLDSTEIN.

"The factors controlling the formation of some derivatives of quinoline, and a new aspect on the problem of substitution in the quinoline series." By E. ROBERTS and E. E. TURNER.

List of Papers, or Abstracts thereof, received between April 7th and May 19th. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"Preparation of some substituted thioanisoles by direct methylthiolation." By H. H. HODGSON and F. W. HANDLEY.

"An investigation of the alleged second isoelectric point of gelatin." By B. N. GHOSH.

"The reduction of arsenic compounds in acid, and in alkaline solution by sodium hyposulphite (hydrosulphite). Production of sodium arseno-hyposulphite." By W. FARMER and J. B. FIRTH.

"Reduction of silver compounds in alkaline solution. Part I. Reduction in presence of aluminium." By W. FARMER and J. B. FIRTH.

"Reduction of silver compounds in alkaline solution. Part II. Hydrolysis of silver nitride." By W. FARMER and J. B. FIRTH.

"Monothioethyleneglycol. Part III. Nitrophenyl thioethers." By G. M. BENNETT and W. A. BERRY.

"The influence of the sulphur atom on the reactivity of adjacent atoms or groups. Part II. A quantitative comparison of the reactivities of chlorine in some β- and γ-chlorosulphides." By G. M. BENNETT and W. A. BERRY.

"The reactions of 1-anilino*cyclo*hexane-1-carboxylic acid. Synthesis of ψ-indoxyl-*spirocyclo*hexane." By R. L. BETTS, R. MUSPRATT, and S. G. P. PLANT.

"Sugar carbonates. Part III. Derivatives of γ-methylfructoside, γ-ethylfructoside, and normal methylfructoside." By C. F. ALLPRESS, W. N. HAWORTH, and J. J. INKSTER.

"The study of lactones derived from simple sugars." By H. D. K. DREW, E. H. GOODYEAR, and W. N. HAWORTH.

"The ternary system barium iodide–iodine–water and the formation of polyiodides." By A. C. D. RIVETT and J. PACKER.

"Substituted diaryl ethers. Part II. Amino-di-*p*-tolyl ethers." By J. REILLY and H. S. B. BARRETT.

"Some sulphur derivatives of substituted benzaldehydes." By H. H. HODGSON and H. G. BEARD.

"Substitution in hexahydrocarbazole derivatives." By J. GURNEY and S. G. P. PLANT.

"Striated photographic records of explosion-waves." By C. CAMPBELL and D. W. WOODHEAD.

"The action of bromine on strontium hydroxide." By K. L. MALHOTRA, H. B. DUNNICLIFF, and H. D. SURI.

"The action of iodine on strontium hydroxide." By K. L. MALHOTRA, H. B. DUNNICLIFF, and R. K. B. BAHL.

"Electrometric and colorimetric dissociation constants of mono- and di-nitro-dihydric phenols." By F. L. GILBERT, F. C. LAXTON, and E. B. R. PRIDEAUX.

"The two *o*-cyanocinnamic acids." By W. DAVIES and H. G. POOLE.

"Acid and salt effects in catalysed reactions. Part IX. A general kinetic method for the determination of the degree of dissociation of water." By H. M. DAWSON.

"The dicarbazyls. Part III. The oxidation of carbazole and *N*-alkylcarbazoles in acid solution." By P. MAITLAND and S. H. TUCKER.

"The nature of the alternating effect in carbon chains. Part XIX. The mechanism of certain migrations." By C. K. INGOLD, E. W. SMITH, and C. C. N. VASS.

"*ortho*-Nitrobenzyl phenyl dimethyl ammonium chloride." By H. BAW.

"The constitution of anthracene." By D. H. PEACOCK and B. K. MENON.

"Melting points of the substituted amides of dibasic acids." By C. R. BARNICOAT.

"The diacyl derivatives of benzidine and *p*-phenylene diamine." By F. J. A. BROGAN.

"Aromatic sulphonyl disulphides." By L. G. S. BROOKER, R. CHILD, and S. SMILES.

"The chemistry of the three-carbon system. Part XII. The effect of positive substituents in the α-position." By G. A. R. KON and B. T. NARAYANAN.

"The preparation of unsaturated ketones from the chlorides of hydroxy acids." By G. A. R. KON and B. T. NARAYANAN.

"The chemistry of the three-carbon system. Part XIII. The effect of bulky substituents and of the *cyclo*heptane ring." By G. A. R. KON and C. J. MAY.

"The constitution of the disaccharides. Part XIII. The γ-fructose residue in sucrose." By W. N. HAWORTH, E. L. HIRST, and V. S. NICHOLSON.

"The heat of adsorption of gases by charcoal." By S. J. GREGG.

"The Reimer–Tiemann reaction with *m*-chlorophenol." By H. H. HODGSON and T. A. JENKINSON.

"The temperature effects of mixing non-aqueous liquids." By W. M. MADGIN, J. B. PEEL, and H. V. A. BRISCOE.

"Low temperature oxidation at charcoal surfaces. Part IV. The active areas for different acids and their relative rates of oxidation." By W. M. WRIGHT.

"Imino-aryl ethers. Part V. The effect of substitution on the velocity of molecular rearrangement." By A. W. CHAPMAN.

"The preparation and hydrolysis of the isomeric β-tolylethyl bromides." By J. B. SHOESMITH and R. J. CONNOR.

"Melting points and heats of crystallisation of homologous series. Part III. Myristic acid derivatives." By W. E. GARNER and J. E. RUSHBROOKE.

"The electroendosmosis of aqueous solutions through a diaphragm of sintered glass powder." By F. FAIRBROTHER and H. VARLEY.

"Aminobenzthiazoles. Part X. The effect of polar substituents on the formation and stability of the bromo-addition compounds of the benzthiazole series and the synthesis of some disubstituted 1-anilinobenzthiazoles." By G. M. DYSON, R. F. HUNTER, and C. SOYKA.

"Aminobenzthiazoles. Part XI. The effect of the atomic volume of the alkyl group on the stability of the bromides of the 5-substituted 1-alkylaminobenzthiazoles." By R. F. HUNTER and E. R. STYLES.

"Investigations in the diphenyl series. Part VI. Note on the configuration of diphenyl derivatives." By F. Bell and P. H. Robinson.

"The action of diazonium salts on pyrones, and their parent substances. Part I." By R. T. Mullen and W. H. Crowe.

"The decomposition of nitrous acid in aqueous solution." By T. W. J. Taylor, E. W. Wignall, and J. F. Cowley.

"Some observations on the determination of surface tension by means of capillary rise. The surface tension of water, ethyl alcohol, boron trichloride, and silicon tetrachloride." By H. Mills and P. L. Robinson.

"The action of the silver salt of ethyl dehydroundecylenate upon alkyl halides." By W. W. Myddleton and R. G. Berchem.

"A new equation for electrode potentials." By M. Meyer.

"The inflammation of mixtures of the paraffins and air in a closed spherical vessel." By G. B. Maxwell and R. V. Wheeler.

"The chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part VIII. The differing effects of the *gem*-dimethyl and *spiro-cyclo*hexane groupings on the direction of blocking of an intra-annular tautomeric system by substitution." By C. K. Ingold and E. A. Seeley.

"The nature of the alternating effect in carbon chains. Part XX. The conditions underlying vicinal substitution in *o*-substituted benzenes containing *op*-orienting groups." By C. K. Ingold and E. W. Smith.

"Note on the estimation of potassium in presence of iodide." By F. S. Hawkins and J. R. Partington.

"The factors controlling the formation of some derivatives of quinoline, and a new aspect on the problem of substitution in the quinoline series." By E. Roberts and E. E. Turner.

"Chemical action at an interface; the production of acidity in neutral salt solutions." By N. V. Achar and F. L. Usher.

"Syntheses of cyclic compounds. Part I. Ethyl $\beta\gamma$-dimethyl butane $\alpha\alpha\delta\delta$-tetracarboxylate and some *cyclo*butane compounds derived therefrom." By I. Vogel.

"*cis–trans*-Isomerism of disulphoxides." By E. V. Bell and G. M. Bennett.

"The mercuration of *o*-nitrophenol." By H. H. Hodgson.

"A new method of (absolute) potentiometric titration." By B. Cavanagh.

"Ionisation and chemical change during slow combustion." By J. A. J. Bennett and E. W. J. Mardles.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, JUNE 16TH, 1927.

BACKEBERG, OTTO GUIDO, University of the Witwatersrand, Johannesburg, South Africa. British. Lecturer in Chemistry. B.A. (Hons.), Oxford, 1923. M.Sc., Johannesburg, 1926. A.I.C., 1924. "The Theory of Indicators," *South African Journal of Science*, Vol. XXI, pp. 243–257. "Alkyl Hypochlorites," *Journal of S.A. Chemical Institute*, January, 1925; "Alkyl Hypochlorites," *J.C.S.*, 1923, p. 2999 (with Dr. F. D. Chattaway); "The Chlorination of Ethyl Alcohol," *J.C.S.*, 1924, p. 1097 (with Dr. F. D. Chattaway). (*Signed by*) J. A. Wilkinson, Henry Stephens, F. D. Chattaway.

BAYLEY, LEONARD, 31, The Crescent, Friern Barnet, N. 11. English. Propaganda Manager to The Hoffmann–La Roche Chemical Works, Ltd., 7 & 8 Idol Lane, E.C. 3. Reasons for wishing to become a Fellow: (1) to be privileged to attend the evening meetings; (2) to have an opportunity of perusing and studying the Society's proceedings and literature; (3) to use the Society's Library. For many years engaged in writing, compiling, and editing printed matter on chemical, pharmaceutical, and medical subjects, and in translating such matter into English from various continental languages. (*Signed by*) J. Langford Moore, Archibald Macpherson, E. T. Neathercoat.

BELL, JAMES, jun., 3, Finnart Terrace, Greenock. British. Research Student, Chemistry Dept., Glasgow University. B.Sc. with 1st Class Hons. in Chemistry, June 1926. Elected A.I.C. 1926. D.S.I.R. Research Student for 1926–27–28. (*Signed by*) G. G. Henderson, T. S. Patterson, R. Wright, David T. Gibson.

BISSELL, WILLIAM JOHN, 863, London Road, Westcliff-on-Sea, Essex. British. Works Chemist. Student at the East London College, 1922–1926. Chemist at the Ipswich Beet Sugar Factory during the 1926–27 Campaign. (*Signed by*) J. R. Partington, W. H. Patterson, F. E. King.

BLELOCH, WILLIAM, "Hazleyshaw," Albemarle St., Kensington, Johannesburg, South Africa. British. Research Student in Chemistry. B.Sc., University of the Witwatersrand. At the present time carrying out research in organic chemistry for the degree of M.Sc., and therefore desirous of keeping in touch with modern developments of the subject. (*Signed by*) Henry Stephen, J. McCrae, J. A. Wilkinson.

BOYD, DONALD WM. PARKER, M.A., "Glensavage," Stillorgan, Co. Dublin. Irish. Chemist and Druggist. Having been a student of chemistry both at Trinity College (Dublin University) and Kevin St. Tech. Schools, Dublin. Candidate has now complete control and charge of the manufacturing laboratory of Messrs. Boileau & Boyd, Ltd., Wholesale Chemists and Druggists, Dublin, and desires admission as Fellow of the Society in order that he may be brought into closer touch with manufacturing chemistry. (*Signed by*) Emil A. Werner, Sydney Young, Kenneth C. Bailey, James Bell.

BROOKER, LESLIE GEORGE SCOTT, 54, Augustine Street, Rochester, N.Y., U.S.A. British. Organic Chemist, Eastman Kodak Coy., Rochester, N.Y. 1st Class Hons. B.Sc. (Lond., 1923). A.I.C. Ph.D. (Lond., 1926). "A Method of Inserting the Thio-aryl Group," Brooker and Smiles, *J.C.S.*, 1926, 1723. (*Signed by*) H. T. Clarke, Samuel Smiles, A. J. Allmand.

CAMPS-CAMPINS, FRANCISCO MIGUEL, 67, Frederick Street, Port of Spain, Trinidad. British Subject. Sugar Technologist and Chemist. B.Sc. (Audubon Sugar School). Superintending Chemist to J. Supple's Sons Pltg. Co.,

Sugar Factory at Bayou Goula, La., U.S.A., and to The American Syrup & Sorghum Co., Fort Smith (Syrup) Factory at Arkansas, U.S.A., during the grinding season. (*Signed by*) P. E. Turner, Joseph de Verteuil, James D. Kettle.

CURJEL, WILLIAM RYLE CLIFFORD, Netherside, Woodbridge, Suffolk. British. Research Student. B.A. (Oxon.), 1st Class Hons. Chemistry. Research Studentship (Oxford), 1926. (With F. D. Chattaway), *J.C.S.*, 1926, p. 3210, "The Crystalline Forms of 5-Nitro-salicylic Acid and of Related Compounds." (*Signed by*) H. L. Bowman, F. D. Chattaway, T. V. Barker.

FILBY, FREDERICK ARTHUR, 378, High St. N., East Ham, London, E. 12. English. Student, entering Secondary School Teaching in September (1927). B.Sc., 2nd Class Hons., London, Chem., 1926. (*Signed by*) J. R. Partington, E. E. Turner, F. E. King.

GEORGE, VICTOR SCOTTHORN, 139, Bearwood Road, Smethwick. British. Analytical and Metallurgical Chemist. Over 14 years' experience as an Analytical Chemist, including 3 years' partnership with J. Lones, F.I.C., Smethwick. I wish to keep in touch with modern research. (*Signed by*) J. Newton Friend, J. Cooper Duff, J. H. Wood.

GOLDSBROUGH, ROBERT EDWIN, Woodside, Great Horkesley, Colchester. British. Managing Director. Managing Director of Goldsbrough Patents Co., Ltd. Inventor of Oil Water Gas Processes and Processes for the Production of Ethylene from Fuel Oil. (*Signed by*) Herbert Harris, A. M. Low, K. C. Browning.

GOODMAN, ALBERT DE BUSSY, Hatchgate, Massetts Rd., Horley, Surrey. British. A.I.C. Student, Battersea Polytechnic. Exams. passed: (1) Cambridge Local; (2) Union of Education, 1st Class Theor. Chemistry; (3) Royal Soc. Arts English; (4) Matriculation; (5) Inter. B.Sc., Chemistry, Physics, and Botany; (6) Honours Course at King's College; (7) A.I.C. passed Pract. Chemistry, French, German, failed Theoretical Chemistry. Experience in Cement Analysis, with H. F. Knight, F.I.C., 14, Old Queen St. (*Signed by*) J. Kenyon, Harold Hunter, J. L. White.

GUPTA, BHABA NATH DAS (Noakhali—a district town in Bengal, India). Indian Hindu. B.Sc., M.B. (Calcutta University). As a medical practitioner, I like to remain in constant touch with the progress of chemistry (especially biochemistry). (*Signed by*) A. C. Sircar, J. C. Ghosh, P. C. Guha.

HARVEY, CECIL OWEN, Government Laboratory, Clement's Inn Passage, Strand, W.C. 2 (31, Camden Square, N.W. 1). British. Assistant Chemist. B.Sc. (London). A.R.C.S. A.I.C. Late Assistant Chemist to Messrs. T. Morson & Son, Ltd., The British Launderers' Research Association, etc. *The Analyst*, 1925, 538; 1926, 238. *Chemistry and Industry*, 1925, 815, 1110; 1926, 233; 1927, 317. (*Signed by*) A. G. Francis, W. Maw, J. S. Carter.

LYLE, WILLIAM CLAUDE, 308, Dumbarton Road, Glasgow, W. 1. British. Research Student, Chemistry Dept., Glasgow University. B.Sc., 1st Class Honours in Chemistry, Glasgow, 1926. A.I.C., elected 1926. Strang-Steel Research Scholar, Glasgow Univ., 1926–27. (*Signed by*) G. G. Henderson, T. S. Patterson, R. Wright, David T. Gibson.

MERRY, JAMES SHANKLAND, 22, Norwood Grove, Liverpool. English. Assistant Chemist and Demonstrator to the Liverpool Borax Co., Ltd. Five years in the Liverpool laboratory of Messrs. William Gossage & Sons, Ltd., doing all kinds of process control analysis. Two months in the Gossage Widnes laboratory. Three months as Assistant Chemist to the Liverpool Borax Co., Ltd. (*Signed by*) George Tate, George S. Irving, Charles A. Kelly.

POULSON, CECIL ARTHUR, "Haverstock," Shawlands, Glasgow. British.

Superintending Engineer for Scotland for Messrs. Wests Gas Improvement Co., Ltd., Manchester. *Present Position :* To advise upon and direct tests to obtain improved results in the carbonisation of coals, and extraction of residuals, together with the manufacture of bye-products from residuals. *Late :* Chief Technical Assistant Engineer and Manager for Messrs. W. G. Bagnall, Ltd., Locomotive Engineers, Stafford. Studied Chemistry for 5½ years at Stafford Technical School. (*Signed by*) Thomas Henry Poulson, Joseph Poulson, Cyril Douglas Birks.

RUMBOLD, JOHN STORROW, 22, Calton Avenue, Wavertree, Liverpool. British. Chemistry Master at the Holt Secondary School, Sefton Park, Liverpool. Special B.Sc. (Lond.), 1st Class Hons. in Chemistry. A.I.C. Formerly Research Chemist with the British Oxygen Co. Works Chemist with the Corby Ironstone Co. Works Chemist with the British Celanese Co. Now engaged in research work at the University of Liverpool and in independent research. (*Signed by*) J. B. Firth, F. C. Laxton, V. J. Occleshaw, A. O. Jones.

SUBRAHMANYAN, VAIDYANATHA, Lecturer in Biochemistry, Indian Institute of Science, Bangalore, India. British Indian. Lecturer in Biochemistry. B.A., University of Madras. "Studies relating to Acetone-producing Organisms," *J. Ind. Inst. Sci.*, 1925; "Biochemistry of Waterlogged Soils" (4 parts), in *J. Ag. Sci.*, 1927; "On New Methods relating to the Estimation of Carbohydrates, Fatty Acids, and Lactic Acid in Soils"; "A Modified Method for Estimating Dissolved Oxygen," etc., etc. (*Signed by*) H. J. Page, Ralph P. Hobson, H. L. Richardson.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

KURABAYASHI, GENSHIRO, The Tokyo Higher Normal College, Koishikawaku, Tokyo, Japan. Japanese. Prof. of Inorganic and Analytical Chemistry, Tokyo Higher Normal College. Graduate of the Tokyo Higher Normal College (1905). Prof. of Inorganic and Analytical Chemistry at the Department of Chemistry, Tokyo Higher Normal College (1911–). Member of the Chemical Society of Japan (1923–). (*Signed by*) Joji Sakurai.

SACHS, EUGENIE, 280, Market Street, Pretoria, S. Africa. British subject. Chemist and Pharmacist. Occupied in making Pharmaceutical preparations in firm of Nathan Sachs, Pretoria, S. Africa. I have also the qualification as a pharmacist of the Pharmaceutical Society of Great Britain. (*Signed by*) H. Lucas.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ARCHBUTT, LEONARD, and DEELEY, RICHARD MOUNTFORD. Lubrication and lubricants. A treatise on the theory and practice of lubrication, and on the nature, properties, and testing of lubricants. 5th edition. London 1927. pp. xxxii + 650. ill. 36*s*. net. (*Recd.* 3/5/27.) From the Authors.

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE. A catalogue of heavy and fine chemicals, raw material, machinery, plant, and

equipment applicable to production industries, standardised, condensed and cross-indexed. Compiled with the co-operation of leading British manufacturers. Edited by DUDLEY MAURICE NEWITT. 3rd edition. London [1927]. pp. 404. ill. (*Reference.*) 15*s*. net. From the Publisher : Mr. Leonard Hill.

DOTY, MARION FOSTER. Selenium : a list of references, 1817–1925. New York 1927. pp. iv + 114. (*Reference.*) $·65.
From Mr. C. Ainsworth Mitchell.

HORSFALL, RONALD S., and LAWRIE, LESLIE GORDON. The dyeing of textile fibres. London 1927. pp. xii + 416. 28*s*. net. (*Recd.* 29/4/27.) From the Publishers : Messrs. Ernest Benn.

IRON AND STEEL INDUSTRY and British Foundryman. Supplement to "The Metal Industry." Vol. I, etc. London 1927 +. (*Reference.*) From the Faraday Society.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. V. Part ii. Berlin 1927. pp. 290 to 528. *M*. 10. (*Recd.* 30/4/27.)
From the Publishers : Herren Urban & Schwarzenberg.

II. *By Purchase.*

COHEN, ERNST. Physico-chemical metamorphosis and some problems in piezochemistry. New York 1926. pp. x + 190. ill. 12*s*. 6*d*. net. (*Recd.* 11/5/27.)

COLLOID SYMPOSIUM MONOGRAPH. Papers presented at the fourth National Symposium on Colloid Chemistry. New York 1926. pp. 378. ill. 27*s*. net. (*Recd.* 25/4/27.)

LA WALL, CHARLES H. Four thousand years of pharmacy : an outline history of pharmacy and the allied sciences. Philadelphia 1927. pp. xvi + 666. ill. 25*s*. net. (*Recd.* 11/5/27.)

LINTON, R. G. Animal nutrition and veterinary dietetics. Edinburgh 1927. pp. xii + 400. ill. 21*s*. net. (*Recd.* 11/5/27.)

NEBLETTE, C. B. Photography, its principles and practice : a manual . . . for use in colleges, technical institutions, and by the advanced student of the science. [New York] 1927. pp. xviii + 644. ill. 30*s*. net. (*Recd.* 11/5/27.)

PARRISH, PERCY, and OGILVIE, ALEXANDER. Artificial fertilisers : their chemistry, manufacture and application. Vol. I. London 1927. pp. 356. ill. 45*s*. net. (*Recd.* 11/5/27.)

ROSS-MACKENZIE, JOHN. A standard manual of brewing and malting and laboratory companion : a practical guide to the art and science of brewing and malting, and to the physical and chemical evaluation of the materials employed. . . . Based on "A handy book for brewers," by H. E. WRIGHT. London 1927. pp. xxii + 412. ill. 45*s*. net. (*Recd.* 11/5/27.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 2nd, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Wilfred Carpmael	June 15th, 1899.	May 31st, 1927.
James David Kettle	Dec. 6th, 1901.	May 20th, 1927.
Edalji Manekji Modi.....	Dec. 7th, 1905.	Sept. 13th, 1924.
William Carleton Williams ...	Feb. 19th, 1874.	May 25th, 1927.

W. H. Hatfield was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

Stephen de Finály, Lónyay-u, 41, Budapest.
David Clarence Rhys Jones, B.Sc., 10, Berkeley Avenue, Levenshulme, Manchester.
Robert Napier Kerr, B.Sc., Ph.D., 22, St. Bernard's Crescent, Edinburgh.
Cyril Dunn Lawrence, B.Sc., 46, Juer Street, Park Road, Battersea, S.W. 11.
Harry Pavion, 4, Brideoak Street, Cheetham, Manchester.

The following papers were read:

"The passivity of metals. Part I. The isolation of the protective film." By U. R. EVANS.

"Studies of valency. Part VIII. The molecular structure of Vernon's dimethyltelluronium salts." By T. M. LOWRY and (MRS.) R. R. GOLDSTEIN.

"The factors controlling the formation of some derivatives of quinoline, and a new aspect on the problem of substitution in the quinoline series." By E. ROBERTS and E. E. TURNER.

Ordinary Scientific Meeting, Thursday, June 16th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of:

	Elected.	Died.
Edward Day Gravill	June 16th, 1887.	May 6th.
Harold McLean Read	May 4th, 1899.	April 23rd.
Gotfred Midgley Taylor	Dec. 7th, 1882.	June 11th.

The PRESIDENT announced that:

1. It had been decided to issue shortly, in separate form, the Faraday Lecture delivered by Prof. Richard Willstätter on May 18th. The price will be one shilling each, and application should be made to the Assistant Secretary.

2. The Annual Reports on the Progress of Chemistry for 1927, Volume XXIV, will be sold at 5*s.* 6*d.* post free to those Fellows who apply by *Christmas Day*, 1927.

3. It had been decided to issue the Abstracts "A" (Pure Chemistry) for 1928, *printed on one side of the page only* at the reduced price of £1 to Fellows who apply to the Assistant Secretary by *Christmas Day*, 1927. A remittance for £1 must accompany the application, and Fellows should state whether they wish to receive the Abstracts gummed, or ungummed. Further notice will be given.

The PRESIDENT then stated that he had the happy duty to perform of making a presentation to Mr. S. E. Carr, to mark the completion of his 25th year as Assistant Secretary. Before making the formal presentation, he asked Dr. Alexander Scott to make a few remarks.

Dr. Scott said that it gave him great pleasure to comply with the President's request, for he had held office for 24 out of the 25 years Mr. Carr had been Assistant Secretary—as Secretary from 1902 to 1904, as Treasurer from 1904 to 1915, and as President from 1915 to 1917—and no one could speak with greater knowledge and authority than he of the services rendered by Mr. Carr to the Society.

The announcement of Mr. Carr's appointment was made in the Annual Report of the Council for 1903 in the following simple words: "After careful consideration, the Council decided to separate the duties of Assistant Secretary from those of the Librarian and Curator, Mr. Steele retaining the latter, whilst Mr. S. E. Carr has been appointed Assistant Secretary." The Council never did an act more timorously, and no Council had ever made a wiser or more successful appointment.

He stated that it was found necessary to undertake a thorough revision of the entire business methods of the Society, and the brunt of this work had fallen upon Mr. Carr and himself, and only they could appreciate what this meant. At this early and trying stage of his career, Mr. Carr fully justified the selection of the Council and proved the value of his business training. Throughout all the

succeeding years and the consequent numerous changes in the Officers and in the personnel of the Committees, there has been only one opinion as to the wisdom of the appointment made 25 years ago. Mr. Carr has thrown his whole soul and energy into everything that he could do to promote the welfare of the Society, utterly regardless of the amount of work any new development might bring upon himself. He would say to those present and to all who know Mr. Carr personally that nothing could have given him greater pleasure and satisfaction than this opportunity of thus testifying to Mr. Carr's inestimable services to the Society.

The PRESIDENT, after expressing his appreciation of Mr. Carr's courtesy and of his devotion to his work, handed him two cheques, one from the Council and the other from Fellows, who had given in addition a "Grandmother" clock and an Album containing the signatures of the Honorary Fellows and the Fellows who had contributed.

Mr. Carr, in expressing his gratitude for the gifts, spoke of his great indebtedness to the Council, and to the Fellows of the Society who had contributed to the presentation. The Album would, he said, be particularly precious, as it would ever serve as a reminder of the intimate and happy associations he had always had with the Honorary Officers and with many of the Fellows. He deeply regretted that the Album did not contain the signatures of Sir William Tilden and Dr. Crossley, recalling that it was Sir William who offered him the appointment and who honoured him with his friendship. Mr. Carr stated how much pleasure it gave him to see present Prof. Thomson, for he was associated with him more than 30 years ago, and Dr. Scott, with whom he had worked for so many years; it was also a very happy coincidence that Dr. Forster should happen to be in London at this time. Again expressing his deep thanks to all those who had contributed to the presentation, Mr. Carr wished to thank especially warmly the Treasurer and those assisting him for the trouble they had so generously taken with regard to the presentation. The appreciation of his services manifested by the generous gifts would be an incentive to him to continue to carry on his work for the Society with enthusiasm and to the utmost of his ability.

Certificates were read for the first time in favour of:

Albert William Kemp Ingram, B.A., 261, High Street, Sheerness.
Arthur Hereward Millard, 8, Westhall Road, Park Lane, Bath.
William Alexander Hugh Oswald, B.A., White Knights, St. George's Hill, Weybridge.
Bijoor Sanjiva Rao, B.A., Indian Institute of Science, Bangalore, India.

Dr. H. Burgess and Mr. F. P. Dunn were elected Scrutators, and

a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

Otto Guido Backeberg, B.A., M.Sc., A.I.C.
Leonard Bayley.
James Bell, jun., B.Sc., A.I.C.
William John Bissell.
William Bleloch, B.Sc.
Donald Wm. Parker Boyd, M.A.
Leslie George Scott Brooker, B.Sc., Ph.D., A.I.C.
Francisco Miguel Camps-Campins, B.Sc.
William Ryle Clifford Curjel, B.A.
Frederick Arthur Filby, B.Sc.
Victor Scotthorn George.
Robert Edwin Goldsbrough.
Albert de Bussy Goodman.
Bhaba Nath Das Gupta, B.Sc., M.B.
Cecil Owen Harvey, B.Sc., A.R.C.S., A.I.C.
Genshiro Kurabayashi.
William Claude Lyle, B.Sc., A.I.C.
James Shankland Merry.
Cecil Arthur Poulson.
John Storrow Rumbold, B.Sc., A.I.C.
Eugenie Sachs.
Vaidyanatha Subrahmanyan, B.A.

The following papers were read :

"Syntheses of cyclic compounds. Part I. Ethyl $\beta\gamma$-dimethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate and some *cyclo*butane compounds derived therefrom." By I. VOGEL.

"A new method of (absolute) potentiometric titration." By B. CAVANAGH.

"*Cis-trans*-isomerism of disulphoxides." By E. V. BELL and G. M. BENNETT.

"Decomposition of some halogenated sulphides, and the nature of the 'polymeric' ethylene sulphides." By E. V. BELL, G. M. BENNETT, and A. L. HOCK.

The Council has made the following Grants from the Research Fund :—

	£	s.	d.
Study of ketones of the type $R_2C{:}CH{\cdot}CO{\cdot}C_2H_5$. (Miss) A. E. Abbott	10	0	0
Orienting influences of certain groups in benzene nuclei. A. W. Baldwin	5	0	0
Studies in aliphatic and cyclic sulphides (*contd.*). G. M. Bennett	10	0	0
Effect of ring formation on substitution and on the reactivity of substituted groups. A. Brewin	10	0	0
Mechanism of isomeric change in aromatic compounds (*contd.*). A. W. Chapman	10	0	0
Determination of structure of certain sesquiterpene derivatives by synthesis. G. R. Clemo	15	0	0
Introduction of substituents into the azo benzene molecule. J. Dexter	5	0	0
Tautomerism of the ketones of the type *cyclo*hexanyl acetone (*contd.*). A. H. Dickins	10	0	0
Synthetic experiments in the sugar group. H. D. K. Drew ...	10	0	0
Isolation of dvi-manganese from manganese-containing compounds (*contd.*). J. G. F. Druce	6	0	0

	£	s.	d.
$\alpha\beta$-Dicyano esters of aliphatic acids. P. K. Dutt	15	0	0
Properties of conjugated compounds. Factors governing additive reactions. J. T. Evans	10	0	0
Syntheses of partially substituted glycerols and other compounds. A. Fairbourne	15	0	0
Equilibria between $\alpha\beta$- and $\beta\gamma$-unsaturated acids (*contd.*). A. A. Goldberg	10	0	0
Experiments in the *iso*quinoline series. R. D. Haworth ...	10	0	0
Studies in the monosaccharide group. E. L. Hirst	10	0	0
Oxidation of sugars and the preparation of reference compounds. D. I. Jones	5	0	0
Formation and nitration of *N*-substituted piperidines. R. J. W. Le Fèvre	5	0	0
Studies in polymerisation. C. W. Long	7	0	0
Condensation of aldehydes with glycine anhydride. P. G. Marshall and W. P. Dickinson	5	0	0
Synthesis of hexoses. S. Peat	5	0	0
Structure of simple sugars. J. H. G. Plant	5	0	0
Effect of the so-called "strainless" rings on the carbon tetrahedral angle (*contd.*). K. A. N. Rao	15	0	0
Structure of sparteine. R. Raper	10	0	0
Relative reactivities of halogens in alkyl halides. H. W. Rudd	3	0	0
Influence of groups and associated rings on the stability of certain ring systems (*contd.*). S. S. G. Sircar	12	10	0
Synthesis of cyclic compounds. I. Vogel	10	0	0
Mechanism of the oxidation of fatty acids by enzymes secreted by mould fungi. T. K. Walker	10	0	0
Spatial structure of *cyclo*paraffins (*contd.*). W. A. Wightman ...	10	0	0
	£263	10	0

THE LIBRARY.

The Library will be closed for Stocktaking from Monday, August 1st, until Saturday, August 13th, 1927 (inclusive). During the following four weeks (August 15th to September 10th), the Library will close daily at 5 p.m.

LIST OF FELLOWS, 1927.

The List of Fellows for 1927 is now in active preparation, and will be supplied to those Fellows who make application to the Assistant Secretary by July 31st, 1927. In order that the new List may be as complete as possible, Fellows are invited to notify any change of address, or other alteration, before that date.

List of Papers, or Abstracts thereof, received between May 19th and June 16th, 1927. (This List does not include the titles of papers

which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"Equilibrium diagram of the system thallium–phosphorous." By Q. A. Mansuri.

"On the condensation of cinnamic acid with resorcinol and pyrogallol." By T. E. Ellison.

"The nature of the sintering of active copper catalysts." By F. H. Constable.

"The action of alkalis on clay." By H. B. Oakley.

"Strychnine and brucine. Part IV." By G. R. Clemo, W. H. Perkin, and R. Robinson.

"Strychnine and brucine. Part V." By J. M. Gulland, W. H. Perkin, and R. Robinson.

"Besson's supposed phosphorus suboxide, P_2O." By L. J. Chalk and J. R. Partington.

"The electronic structure of atoms. Part I. The periodic classification." By J. D. M. Smith.

"The oxidation of nitrophenylcyanoacetates. Part II." By A. Fairbourne and H. R. Fawson.

"Gold and mercury derivatives of 2-thiolglyoxalines. Mechanism of the oxidation of 2-thiolglyoxalines to glyoxalines." By I. E. Balaban and H. King.

"The preparation of 4-hydroxycoumarin derivatives." By I. M. Heilbron and D. W. Hill.

"Styrylpyrylium salts. Part IX. Colour phenomena associated with benzonaphtha- and dinaphtha-*spiro*pyrans." By R. Dickinson and I. M. Heilbron.

"The absorption spectrum of ergosterol, in relation to the photosynthetic formation of vitamin-*D*." By R. A. Morton, I. M. Heilbron, and E. D. Kamm.

"Organic compounds of arsenic. Part III. Orthotriphenylene diarsine." By N. P. McCleland and J. B. Whitworth.

"Chlorocamphoranilic acids and chlorophenyl camphorimides." By M. Singh and R. Singh.

"The isomeric hydroxybenzyldimethylamines." By E. Stedman.

"A synthesis of rutaecarpine." By Y. Asahina, R. H. F. Manske, and R. Robinson.

"Methyl mercuric halides and hydroxide." By L. E. Hinkel and T. H. Angel.

"The oxidation of triacontane." By F. Francis and N. E. Wood.

"A new form of thermostat and observation tubes for polarimetric work." By T. S. Patterson.

"Molecular structure in solution. Part II. The refractive indices

and surface tension of aqueous solutions of cobalt chloride and hydrochloric acid." By O. R. Howell.

"A synthesis of safrole and *o*-safrole." By W. H. Perkin and V. M. Trikojus.

"Acid and salt effects in catalysed reactions. Part X. The hydrolysis of ethyl acetate with acetic acid as catalyst." By H. M. Dawson and W. Lowson.

"Experiments on the synthesis of anthocyanins. Part III." By A. Robertson and R. Robinson.

"The catalytic hydrogenation of different types of unsaturated compounds. Part II. The hydrogenation of conjugated systems." By S. V. Lebedev and A. O. Yakubchik.

"The systems B_2O_3–SO_3–H_2O and B_2O_3–P_2O_5–H_2O." By M. Levi and L. F. Gilbert.

"Studies in the coumarin series. Part I. The action of the Grignard reagent upon substituted coumarins." By I. M. Heilbron and D. W. Hill.

"The intermolecular condensation of styryl methyl ketones. Part I." By R. Dickinson, I. M. Heilbron, and F. Irving.

"Reactions of sodium compounds of aromatic ketones. Part I. Synthesis of triarylcarbinols and of triarylmethane dyes." By E. H. Rodd and F. W. Linch.

"Reactions of sodium compounds of aromatic ketones. Part II. Their reaction with methyl and methylene groups and their products of decomposition." By E. H. Rodd and F. W. Linch.

"Molecular volumes at absolute zero. Part I. Density as a function of temperature." By S. Sugden.

"Molecular volumes at absolute zero. Part II. Zero volumes and chemical composition." By S. Sugden.

"The action of hydrazines on semicarbazones. Part III." By W. Baird and F. J. Wilson.

"Nitro-derivatives of the homopyrocatechol ethers." By A. E. Oxford.

"The thermal dissociation of carbonyl chloride." By H. Ingleson.

"The isomerism of the oximes. Part XXXI. The furfuraldoximes and 2-methoxy- and 4-methoxy-1-naphthaldoximes." By O. L. Brady and R. F. Goldstein.

"Syntheses of glucosides. Part I. The synthesis of indican." By A. Robertson.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ASKINSON, [GEORGE WILLIAM]. Le manuel du parfumeur. 4th French edition. By RENÉ SORNET. Paris 1927. pp. vi + 142. ill. 18 *fr.* (*Recd.* 15/6/27.)
From the Publishers: MM. Gauthier Villars et Cie.

BRENCHLEY, WINIFRED ELSIE. Inorganic plant poisons and stimulants. 2nd edition. Cambridge 1927. pp. x + 134. ill. 10*s.* 6*d.* net. (*Recd.* 30/5/27.) From the Author.

CAVEN, ROBERT MARTIN. Atoms and molecules: being Part I and Chapter XII of "The foundations of chemical theory." London 1927. pp. viii + 142. ill. 7*s.* net. (*Recd.* 3/6/27.)
From the Publishers: Messrs. Blackie & Son.

MARTIN, ARTHUR JOHN. The activated sludge process. London 1927. pp. xiv + 416. ill. 30*s.* net. (*Recd.* 13/6/27.)
From the Author.

SAUNDERS, VIVIAN T. The polarimeter: a lecture on the theory and practice of polarimetry. London [1927]. pp. 30. ill. 1*s.* 6*d.* net. (*Recd.* 24/5/27.) From the Publishers: Messrs. Adam Hilger.

STEVENS, HENRY POTTER. The paper mill chemist. 3rd edition. London 1926. pp. viii + 317. ill. 10*s.* 6*d.* net. (*Recd.* 24/5/27.) From the Author.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. VI. Part iv. Berlin 1927. pp. 721 to 960. *M.* 10. (*Recd.* 8/6/27.)
From the Publishers: Herren Urban & Schwarzenberg.

TWYMAN, FRANK. Two lectures on the development and present position of chemical analysis by emission spectra. London [1927]. pp. 43. ill. 2*s.* 6*d.* net. (*Recd.* 24/5/27.)
From the Publishers: Messrs. Adam Hilger.

[UNITED STATES] NATIONAL RESEARCH COUNCIL. A survey of American chemistry. Vol. I, July 1, 1925 to July 1, 1926. Edited by WILLIAM J. HALE in co-operation with CLARENCE JAY WEST. New York 1927. pp. 258. (*Reference.*) From the Editors.

II. *By Purchase.*

BAUD, PAUL. Chimie industrielle. La grande industrie chimique; les métalloïdes et leur composés; les métaux et leurs sels; industries organiques. 2nd edition. Paris 1927. pp. xii + 1022. ill. 100 *fr.* (*Recd.* 17/6/27.)

BELL, SIR WILLIAM JAMES. The Sale of Food and Drugs Acts, . . . with notes and cases. 7th edition. By CHARLES F. LLOYD and

R. A. Robinson. London 1923. pp. xxvi + 374 + 54. 15*s*. net. (*Recd*. 21/5/27.)

Blasdale, Walter Charles. Equilibria in saturated salt solutions: a summary of the results of the study of the heterogeneous equilibria which exist in aqueous solutions of electrolytes. New York 1927. pp. 198. ill. 19*s*. net. (*Recd*. 16/5/27.)

Dammer, Bruno, and Tietze, Oskar. Die nutzbaren Mineralien mit Ausnahme der Erze und Kohlen. 2nd edition. Vol. I. Stuttgart 1927. pp. xx + 554. ill. *M*. 35·40. (*Recd*. 21/5/27.)

Foster, William. The romance of chemistry. New York 1927. pp. xvi + 468. ill. 12*s*. 6*d*. net. (*Recd*. 8/6/27.)

Fränkel, Sigmund. Die Arzneimittel-Synthese. Auf Grundlage der Beziehungen zwischen chemischem Aufbau und Wirkung. 6th edition. Berlin 1927. pp. vii + 935. *M*. 93. (*Recd*. 2/6/27.)

Gottlob, [Kurt]. Technology of rubber. Translated from the German edition of 1925 by Joseph L. Rosenbaum. London 1927. pp. xvi + 350. ill. 42*s*. net. (*Recd*. 18/5/27.)

Haas, Arthur. Atomic theory: an elementary exposition. Translated by Terence Verschoyle. London 1927. pp. xiv + 222. ill. 10*s*. 6*d*. net. (*Recd*. 18/5/27).

Haber, Fritz. Aus Leben und Beruf: Aufsätze, Reden, Vorträge. Berlin 1927. pp. vii + 173. ill. *M*. 5·70. (*Recd*. 2/6/27.)

Hall, Archibald John. Textile bleaching, dyeing, printing and finishing machinery. London 1926. pp. 320. ill. 50*s*. net. (*Recd*. 16/5/27.)

Herzog, Reginald Oliver. [Editor.] Chemische Technologie der organischen Verbindungen. 2nd edition. Heidelberg 1927. pp. xii + 997. ill. *M*. 70. (*Recd*. 21/5/27.)

Hevesy, Georg von. Die seltenen Erden vom Standpunkte des Atombaues. (Struktur der Materie in Einzeldarstellungen.) Berlin 1927. pp. vii + 140. ill. *M*. 10·20. (*Recd*. 2/6/27.)

Hückel, Walter. Katalyse mit kolloiden Metallen. (Kolloidforschung in Einzeldarstellungen.) Leipzig 1927. pp. viii + 86. ill. *M*. 6. (*Recd*. 18/5/27.)

Hund, Friedrich. Linienspektren und periodisches System der Elemente. (Struktur der Materie in Einzeldarstellungen.) Berlin 1927. pp. vi + 221. ill. *M*. 16·20. (*Recd*. 2/6/27.)

Kolthoff, I. M. Konduktometrische Titrationen. Dresden 1923. pp. vii + 94. ill. *M*. 2·75. (*Recd*. 25/5/27.)

Meyer, Stefan, and Schweidler, Egon. Radioaktivität. 2nd edition. Leipzig 1927. pp. x + 722. ill. *M*. 36. (*Recd*. 25/5/27.)

Möbius, Martin. Die Farbstoffe der Pflanzen. Berlin 1927. pp. vii + 200. ill. *M*. 14·50. (*Recd*. 21/5/27.)

MOOKERJI, BHUDEB. Rasa-jala-nidhi, or, Ocean of Indian chemistry and alchemy. Vol. I. Compiled in Sanskrit with English translation. Calcutta [1926]. pp. xxiv + 350 + vi. 15*s.* net. (*Recd.* 18/5/27.)

PULLIN, V. E., and WILTSHIRE, W. J. X-rays past and present. London 1927. pp. 230. ill. 12*s.* 6*d.* net. (*Recd.* 18/5/27.)

SMITH, EDGAR FAHS. Old chemistries. New York 1927. pp. xii + 90. ill. 12*s.* 6*d.* net. (*Recd.* 9/6/27.)

STRACHE, HUGO, and ULMANN, HEINRICH. Leitfaden der Technologie der Brennstoffe. Leipzig 1927. pp. x + 471. ill. *M.* 24·40. (*Recd.* 8/6/27.)

THAYSEN, AAGE CHRISTIAN and BUNKER, HENRY JAMES. The microbiology of cellulose, hemicelluloses, pectin and gums. London 1927. pp. viii + 364. ill. 25*s.* net. (*Recd.* 11/5/27.)

TOLMAN, RICHARD C. Statistical mechanics with applications to physics and chemistry. New York 1927. pp. 334. 29*s.* 6*d.* (*Recd.* 13/6/27.)

WORLD POWER CONFERENCE. Transactions of the Basle Sectional meeting 1926. 2 vols. Basel [1927]. pp. xxxii + 1258, xxiv + 1538. ill. (*Reference.*) £5 net.

III. *Pamphlets.*

BARTON, FRANCIS RICKMAN. Nickel coinage. London [1926]. pp. iv + 50. ill.

BUTLER, JOE B. Descriptive bibliography on oil and fluid flow and heat transfer in pipes. (From *Bull. Univ. Missouri School of Mines and Metallurgy, Tech. Series*, 1926, **9**.)

CARPENTER, HENRY CORT HAROLD. Methods of growing large metal crystals: being the fourth Sorby Lecture, delivered on Friday, October 22nd, 1926. [Sheffield 1927.] pp. 31. ill.

COWARD, HUBERT FRANK [and others]. The explosibility of methane and natural gas. (Bulletin 30, Mining and Metallurgical Investigations.) Pittsburgh 1926. pp. viii + 42. ill.

ELWORTHY, R. T. Helium in Canada. (Canada, Department of Mines. Mines Branch No. 679.) Ottawa 1926. pp. iv + 64. ill.

HANCOCK, GEORGE CHARLES. A report on the occurrence of glass fragments in foods packed in glass containers. (*Ministry of Health Reports on Public Health and Medical Subjects*, No. 37.) London 1927. pp. iv + 36. ill.

——— Report on an outbreak of illness at Poplar suspected to be due to local pollution of the water supply. (*Ministry of Health Reports on Public Health and Medical Subjects*, No. 41.) London 1927. pp. iv + 27. ill.

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—— —— Paper No. 34. Safety in mines research station, Buxton. A description. London 1927. pp. 45. ill.

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—— The determination of sulphur dioxide in foods. (*Ministry of Health Reports on Public Health and Medical Subjects,* No. 43.) London 1927. pp. vi + 56. ill.

PHARMACEUTICAL SOCIETY OF GREAT BRITAIN. Pharmacological Laboratories. First annual report, 1926. London [1927]. pp. 7.

ROTHAMSTED CONFERENCES. I. The growing of lucerne. Report of a conference held at Rothamsted on January 27th, 1926. London 1926. pp. 32.

—— II. The culture and manuring of fodder crops. Report of a conference held at Rothamsted on March 30th, 1926. London 1926. pp. 40.

—— III. Green manuring, its possibilities and limitations in practice. Report of a conference held at Rothamsted on December 10th, 1926. London 1927. pp. 39.

—— IV. The culture and manuring of sugar-beet. Report of a conference held at Rothamsted on January 19th, 1927. London 1927. pp. 56.

RUSSELL, SIR EDWARD JOHN [and others]. The manuring of potatoes. (From the *J. Ministry Agric.*, 1926, 32.)

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. Co-operative industrial research: an account of the work of research associations under the Government scheme. London 1927. pp. viii + 46. ill.

—— Report of the Stone Preservation Committee. London 1927. pp. iv + 33. ill.

—— *Building Research.* Special Report No. 9. Limes and lime mortars. By ALFRED DENYS COWPER. London 1927. pp. vi + 81. ill.

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Engineering Research.* Special Report No. 1. Properties of materials at high temperatures. I. Mechanical properties of Armco Iron, 0·17 per cent. carbon steel, and 0·24 per cent. carbon steel, with special reference to creep. By H. J. TAPSELL and W. J. CLENSHAW. London 1927. pp. viii + 60.

—— *Food Investigation.* Special Report No. 30. Gas storage of fruit: the use of artificial atmospheres of regulated composition . . . for the purpose of preserving fresh fruit during overseas transport or in land stores. By FRANKLIN KIDD, CYRIL WEST, and M. N. KIDD. London 1927. pp. viii + 85. ill.

—— *Fuel Research.* Technical Paper No. 16. The primary decomposition of coal. 1. The temperature of initial decomposition. By JAMES GRIEVE KING and ROBERT ERNEST WILLGRESS. London 1927. pp. vi + 19. ill.

TATTERSFIELD, FREDERICK, GIMINGHAM, CONRAD THEODORE, and MORRIS, H. M. Studies on contact insecticides. Parts I to IV. (From the *Ann. Applied Biol.*, 1925–26, **12–13.**)

UNION INTERNATIONALE DE LA CHIMIE PURE ET APPLIQUÉE. Rapport du Comité de Travail de Réforme de la Nomenclature de Chimie Minérale. Paris 1926. pp. 20.

WANDER, GEORG. Über das "Hesperidin" einiger Pflanzen. Bern 1925. pp. iv + 72 + 8 plates.

[WAR OFFICE.] *Research Department, Woolwich.* R.D. Report No. 67. The influence of molybdenum on medium carbon steels containing nickel and chromium. [By J. A. JONES.] London 1927. pp. 59. ill.

WEIDERPASS, N., and KOGERMAN, P. Über die Anwendbarkeit der Brennschieferöl-Phenolate zur Holzkonservierung. (From the *Sitz. Nat.-Ges. Univ. Tartu*, 1926, **33.**)

WELCH, MARCUS BALDWIN, and COOMBS, FRANK ANDREW. The principal tanning materials of Australia, and their leather forming properties. (*Sydney Technological Museum Bulletin*, No. 10.) 1926. pp. 20 + 7 plates.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, October 20th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
Svante August Arrhenius (Honorary Fellow)	Jan. 20th, 1898.	Oct. 2nd, 1927.
George H. Bostock	June 16th, 1881.	August 1st, 1927.
Benjamin A. Burrell	May 4th, 1882.	July 6th, 1927.
Madanlal J. Gajjar	June 20th, 1912.	July 25th, 1926.
Cuthbert C. Gibbes	Feb. 6th, 1890.	August 25th, 1927.
Alfred J. Gregory	June 18th, 1891.	July 14th, 1927.
Archibald Liversidge	Nov. 7th, 1872.	Sept. 26th, 1927.
Wallace C. Nickels	Dec. 5th, 1889.	July 5th, 1927.
Henry R. Procter	June 15th, 1871.	August 17th, 1927.
Stanley E. Pusey	Feb. 17th, 1927.	May 23rd, 1927.
John T. Sheard	June 16th, 1887.	July 20th, 1927.
Herbert Trewby	March 15th, 1888.	Oct. 19th, 1926.

and stated that the following resolution had been passed by the Council at its Meeting held that afternoon :

> The Council desires to express its deep sorrow at the death of Svante August Arrhenius, who had been a distinguished Honorary Fellow of the Society for nearly twenty years.
>
> The Council records its sense of the irreparable loss the Science of Chemistry has sustained throughout the world, and offers to Madame Arrhenius its warmest sympathy in her bereavement.

It was announced that :

1. Sir Joseph J. Thomson, O.M., F.R.S., Master of Trinity College, Cambridge, had been proposed by the Council as an Honorary Fellow of the Society, and that a ballot for his election would be held at the next Ordinary Scientific Meeting on November 3rd.

2. The Jubilee Dinner of the Institute of Chemistry would be held on Thursday, December 15th, and the Council had decided to abandon the Ordinary Scientific Meeting arranged for that evening.

3. The following address had been sealed and would be presented on the occasion of the Marcelin Berthelot Centenary Celebrations to be held in Paris, October 23rd to 26th, 1927, and that the Society would be represented by the President, Professor H. Brereton Baker, Mr. A. Chaston Chapman, and Professor C. S. Gibson :—

The Chemical Society
to
Le Comité Marcelin Berthelot.

On the occasion of the celebration of the Centenary of the birth of Marcelin Berthelot, we, the President, Council, and Fellows of the Chemical Society, desire to join with you, his countrymen, in paying homage to the memory of the man whose name stands as a symbol for the lifelong pursuit of knowledge in the cause of truth and of civilisation.

In Berthelot we honour the man who first explained the ethereal salts and showed the rôle of Glycerin as a "triatomic" alcohol; who proved that chemical actions might proceed both directly and inversely until an equilibrium was reached; who laboured for years at thermo-chemistry to build up our science on the sure foundation of mechanical laws; who startled us by the explosion-wave; who charmed us with the origins of Alchemy.

But above all we are indebted to Berthelot as the man who first opened to us a new world of Synthetic Organic Chemistry. We are proud to remember that in 1860 our Society honoured itself and him by electing him an Honorary Fellow, and that we possess in our Journal the record of that brilliant experimental lecture in which he showed us how to "forge the first links of the extended chain of organic compounds by methods belonging purely to mineral chemistry."

We look back on Berthelot as one of the great pioneers of Science. In all his explorations he ever sought for the origins of things; he never rested until he discovered the principles underlying the chemical changes he studied.

We of a younger generation who follow his footsteps recognise the master-mind in all his researches; we deeply feel the inspiration of his genius.

Signed on behalf of the Chemical Society,

H. B. Baker, *President.*
Jocelyn Thorpe, *Treasurer.*
T. Slater Price, C. S. Gibson, } *Secretaries.*
F. G. Donnan, *Foreign Secretary.*

(L.S.)

Sealed in Council this Seventh Day of July, One Thousand Nine Hundred and Twenty-seven.

The following were formally admitted Fellows of the Chemical Society: L. Bayley, F. A. Filby, F. G. Soper, R. P. Linstead, W. A. Berry, L. H. N. Cooper, G. C. L. Griffin, G. H. Locket.

Certificates were read for the first time in favour of:

Stanley Birks, B.A., The Limes, High View Avenue, Grays.
George Edward Kevin Blythe, B.Sc., Ph.D., 20, Pantygwydr Road, Uplands, Swansea.
Charles Nightingale Clay, B.Sc., A.I.C., 81, Cromwell Road, S.W. 7.
Philip Dalton Coppock, B.Sc., M.Sc.Tech., 50, Albany Road, Victoria Park, Manchester.
Benjamin John Corder, Rev., B.A., The Rectory, Radnage, High Wycombe.
Herbert England, 22, Queens Road, Harrogate.
Robert Railton Fitzgerald, 68, Bath Row, Birmingham.
Horace Leonard Gerry, Lyndale, Queen's Park, Chester.
Thomas Joseph Glover, M.Sc., Ph.D., 40, Curzon Street, South Circular Road, Dublin.
Mariam Puthenparampil Gommen, B.A., 59, Tregunter Road, West Brompton, S.W. 10.
Charles Robert Harington, M.A., Ph.D., 2, The Greenway, Gerrard's Cross.
Edgar Albert Hayman, 100, Doyle Gardens, Harlesden, N.W. 10.
Herbert Richard Hussey, 31, Thornbury Avenue, Southampton.
John William Thomas Jones, A.R.C.S., 112, Gaskarth Road, S.W. 12.
Reginald Benjamin King, B.Sc., 52, Mostyn Road, Merton Park, S.W. 19.
Zenjiro Kitasato, D.Sc., Chemical Department, The University, Manchester.
Frederic Goronwy Kny-Jones, B.Sc., 1, Linley Road, Bruce Grove, N. 17.
John McBride, Uzina Sinimbri, São Miguel de Campos, Alagôas, Brazil.
James Younger Macdonald, B.A., 17, Learmonth Gardens, Edinburgh.
James Eric McNeil, B.Sc., Claremont, Lake Road East, Cardiff.
David Owen Meredith, P.O. Box AA-B, Hobart, Tasmania.
Shinzo Murakami, Chemical Department, The University, Manchester.
Ryuzaburo Nodzu, D.Sc., Chemical Department, The University, Manchester.
Gordon Perrins, The Royal Infirmary, Edinburgh.
Mata Prasad, D.Sc., Royal Institute of Science, Bombay.
Walter Desmond Raymond, B.Sc., Chemical Laboratory, Baghdad.
Albert Ernest Robinson, 14, Brentwood Terrace, Armley, Leeds.
William Dallas Scott, A.R.C.S., Eldercroft, Cassio Road, Watford.
Ian Campbell Somerville, B.Sc., Ph.D., 319, Ryers Avenue, Cheltenham, Pa., U.S.A.
Robert Walton, The Mill House, Langford, Maldon, Essex.

Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

Paul Nicholas Leech, A.B., Sc.M., Ph.D., 1513, Asbury Avenue, Winnetka, Ill., U.S.A.
Otto Ruff, Dr.Phil., Dr.Ing., Borsigstrasse 23, Breslau, Germany.

The following papers were read:

"Studies of dynamic isomerism. Part XXIV. Neutral salt action in mutarotation." By T. M. LOWRY and G. F. SMITH.

"Studies of dynamic isomerism. Part XXV. The mechanism of catalysis by acids and bases." By T. M. LOWRY.

"10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. Part V. The general method of synthesis and determination of constitution." By C. S. GIBSON and J. D. A. JOHNSON.

"On active nitrogen. Part IV. The independence of the afterglow and chemical properties of active nitrogen." By E. J. B. WILLEY.

LECTURE.

Professor W. A. Bone's lecture entitled "Gaseous Combustion at High Pressures" will be delivered in the Rooms of the Society on Thursday, November 24th, 1927, at 8 p.m.

Owing to limited accommodation only Fellows will be admitted.

ANNUAL REPORTS.

The price of the Annual Reports for 1927, Volume XXIV, will be 5*s.* 6*d.* to those Fellows who apply by Christmas Day, 1927. Application should be made to the Assistant Secretary, and must be accompanied by a remittance.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms obtainable from the Assistant Secretary, must be received on or before Thursday, December 1st, 1927. Applications from Fellows will receive prior consideration.

All persons who received Grants in December, 1926, or in December of any previous year, whose accounts have not been closed by the Council, are reminded that Reports must be returned by December 1st.

ERRATUM.

Proceedings 1927, p. 70, line 8 from bottom, *for* "timorously" *read* "timeously."

List of Papers, or Abstracts thereof, received between June 16th and October 20th, 1927. (This List does not include the titles of

papers which have been read at an Ordinary Scientific Meeting or which have appeared in the Journal.)

" Bis-semidine inversion in aromatic dihydrazo-compounds." By P. C. GUHA and H. K. BANERJEE.

" The composition of bleaching powder. Part I." By E. A. O'CONNOR.

" A contribution to the stereochemistry of tervalent nitrogen." By J. G. JACKSON and J. KENNER.

" The influence of alkalis on the coagulation of silica and clay suspensions." By H. B. OAKLEY.

" The absorption spectra of various alkaloids and their salicylates and of other derivatives of salicylic acid." By J. E. PURVIS.

" The halogenation of *p*-hydroxydiphenylamine. Part II." By A. E. BRADFIELD, L. H. N. COOPER, and K. J. P. ORTON.

" The chemistry of the glutaconic acids. Part XXII. Synthesis of Δ^2-tetrahydro*iso*phthalic acid." By W. M. DUFFIN, E. H. FARMER, and H. L. RICHARDSON.

" The active agent in aqueous bromination." By A. W. FRANCIS.

" A study of the anomalous rotatory dispersion of configuratively related compounds." By C. E. WOOD and S. D. NICHOLAS.

" Anomalous rotatory dispersion from the standpoint of the Drude equation." By C. E. WOOD and S. D. NICHOLAS.

" Rotatory dispersion. Intersections of dispersion curves and of temperature rotation curves." By C. E. WOOD and S. D. NICHOLAS.

" The rotatory dispersion of optically active co-ordination compounds." By C. E. WOOD and S. D. NICHOLAS.

" Some molecular compounds of copper and nickel salicylates." By W. E. HAMER.

" A comparison of the reaction of chromyl chloride with various substituted toluenes." By J. B. SHOESMITH, R. J. CONNOR, and A. C. HETHERINGTON.

" Varying valency of platinum with respect to mercaptanic radicals. Part V. Tervalency and quinquevalency of platinum." By P. C. RÂY.

" Beryllium dialkyls." By H. GILMAN and F. SCHULZE.

" Hydration of cyclic compounds under pressure in presence of osmium and other catalysing agents (catalysers)." By V. S. SADIKOV and A. K. MIKHAILOV.

" The critical temperature of boron trichloride and silicon tetrachloride." By T. W. PARKER and P. L. ROBINSON.

" Organic derivatives of silicon. Part XXXIII. An amorphous variety of octaphenyl*cyclo*silicotetrane." By F. S. KIPPING.

" Organic derivatives of silicon. Part XXXIV. The action of sodium on diphenylphenoxysilicyl chloride." By F. S. KIPPING.

" Organic derivatives of silicon. Part XXXV. The preparation of diphenylsilicon dichloride : Grignard ether and its action on silicon tetrachloride." By F. S. KIPPING and A. G. MURRAY.

" The dichromate reaction as a method for the quantitative estimation of certain aliphatic and aromatic substances." By H. ARK.

" An examination of a method of estimating the iron and sulphur in compounds of these elements." By P. L. ROBINSON, L. A. SAYCE, and J. STEVENSON.

" The reaction between monohydrated ferric oxide and hydrogen sulphide at 100°." By T. G. PEARSON and P. L. ROBINSON.

" A simple form of automatic syphon." By D. C. HARRISON.

"The hydrolysis of solutions of sodium palmitate as measured by extraction with *p*-xylene." By J. W. McBain and R. Buckingham.

"The effect of electrolytes upon the viscosity of solutions of sodium palmitate." By J. W. McBain, H. J. Willavoys, and H. Heighington.

"On a new series of double sulphates of the copper–magnesium group and the sulphonium bases. Part II." By P. C. Rây and N. Rây.

"The action of potassium cyanide upon chloral." By F. D. Chattaway.

"The condensation of *o*-aminothiophenol with $\alpha\beta$-unsaturated acids." By W. H. Mills and J. B. Whitworth.

"The interaction of chloral and aryl hydrazines." By F. D. Chattaway and R. Bennett.

"The alkylation of α-cyano-β-alkylacrylic esters and of α-phenyl-β-alkylacrylic nitriles." By J. A. McRae and R. H. F. Manske.

"Substitution products of 3-nitro- and 3-amino-diphenyl." By W. Blakey and H. A. Scarborough.

"The complex salts of nickel with various aliphatic diamines." By F. G. Mann.

"Substitution products of 4-hydroxybenzophenone and of its methyl ether." By W. Blakey, W. I. Jones, and H. A. Scarborough.

"Molecular structure in solution. Part III. The electrical conductivities of aqueous solutions of cobalt chloride and hydrochloric acid." By O. R. Howell.

"The electroendosmosis of aqueous solutions through glass diaphragms." By H. C. Hepburn.

"The orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. Part II. The nitration of 1-benzylpiperidine and of some related substances." By A. Pollard and R. Robinson.

"Aromatic thionyl and chlorothionyl derivatives. Part III. Some reactions of thionylalizarin." By A. Green.

"On the conjugated trialkyl sulphonium double sulphates of the copper–magnesium group." By P. C. Rây and N. N. Rây.

"Substituted diaryl ethers. Part II. The Friedel and Crafts reaction applied to di-*p*-tolyl ether." By J. Reilly and P. J. Drumm.

"The union of benzoylacetonitrile with organic bases in the presence of salicylaldehyde. Part II." By P. Krishnamurti.

"A note on the thermal dissociation of strontium carbonate." By E. O. Jones and M. L. Becker.

"Halogenation of phenols. Part II. Iodination." By F. G. Soper and G. F. Smith.

"The orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. Part III. The nitration of benzyl-*m*-nitrophenylsulphone." By B. Chatterjee and R. Robinson.

"The orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. Part IV. The nitration of ω-toluenesulphonic acid and of ω-toluenesulphonyl chloride." By A. C. Bottomley and R. Robinson.

"7-Hydroxy-3-phenylcoumarin." By W. Baker.

"The activity theory of reaction velocity. The interaction of *N*-chloroacetanilide and hydrochloric acid." By F. G. Soper and D. R. Pryde.

"The isomerism of the oximes. Part XXXII. Hydrosulphates." By O. L. Brady and A. D. Whitehead.

"A new synthesis of hydrastic acid." By T. S. Stevens and M. C. Robertson.

"The preparation of triacetonamine-hydrate." By F. FRANCIS.
"The condensation of certain β-ketonic esters with o-hydroxymonostyryl ketones." By R. HILL.
"Studies in the sterol group. Part I. The effect of heat on cholesterol and the structure of cholesterilene." By I. M. HEILBRON and W. A. SEXTON.
"Studies in the sterol group. Part II. The absorption spectra of some cholesterol derivatives." By I. M. HEILBRON, R. A. MORTON, and W. A. SEXTON.
"A simple method of finding the true shape and dimensions of a gas molecule at normal temperature and pressure." By A. SKINNER.
"The reactions between oxygen and coal." By W. FRANCIS and R. V. WHEELER.
"A note on Pregl's universal filling applied to combustions on a macro-scale." By W. DAVIES.
"A comparison of the activating effect of the nitro, sulphonic acid, and carboxylic acid groups." By W. DAVIES and E. S. WOOD.
"The formation of organic periodic structures." By M. COPISAROW.
"An *X*-ray examination of saturated dicarboxylic acids and amides of the fatty acid series." By E. HENDERSON.
"A general method for the preparation of carbocyanine dyes." By F. M. HAMER.
"The chemical nature of precipitated basic cupric carbonate." By J. R. I. HEPBURN.
"Investigations on the reactivity of halogens in various types of naphthalene derivatives. Part I." By J. B. SHOESMITH and H. RUBLI.
"The sulphonation of glyoxalines. Part III." By G. R. BARNES and F. L. PYMAN.
"Quaternary salts in the benzoselenazole series." By L. M. CLARK.
"A double compound of chromic and hydrogen chlorides." By J. R. PARTINGTON and S. K. TWEEDY.
"The viscosities of chromic anhydride solutions." By J. R. PARTINGTON and S. K. TWEEDY.
"Some effects of the distribution of current density over an electrode." By E. S. HEDGES.
"Properties of conjugated compounds. Part III. The bearing of hexatriene chemistry on the reactive form of conjugated hydrocarbons." By E. H. FARMER, B. D. LAROIA, T. M. SWITZ, and J. F. THORPE.
"The dimorphism of 2-chloro-4-acetamidotoluene." By M. SCHOFIELD.
"Investigations on the reactivity of halogens in various types of naphthalene derivatives. Part II." By J. B. SHOESMITH and H. RUBLI.
"The mechanism of the formation of citric and oxalic acids from sugars by *Aspergillus niger*." By T. K. WALKER, V. SUBRAMANIAM, and F. CHALLENGER.
"The acetylation of cellulose." By H. J. P. VENN.
"Reduction of nitrites, nitrates, and nitric acid with magnesium amalgam—a new method of preparing hyponitrites and preparation of some new hyponitrites." By P. NEOGI and B. L. NANDI.
"The Reimer–Tiemann reaction with *m*-bromo- and *m*-iodo-phenol." By H. H. HODGSON and T. A. JENKINSON.
"The action of tolylhydrazines upon dihydroxytartaric acid." By F. D. CHATTAWAY and W. G. HUMPHREY.
"Syntheses in the indole series. Part II. 5 : 6-Benzo-4-carboline and its derivatives." By W. O. KERMACK and R. H. SLATER.

"A new stereoisomeride (*trans*-) of hexahydrocarbazole." By J. GURNEY, W. H. PERKIN, and S. G. P. PLANT.

"A physico-chemical study of lactones derived from simple sugars." By S. R. CARTER, W. N. HAWORTH, and R. A. ROBINSON.

"The constitution of the disaccharides. Part XVI. Cellobiose." By W. N. HAWORTH, C. W. LONG, and J. H. G. PLANT.

"Equilibrium in the system $CuSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 37·5°. A correction." By R. M. CAVEN and W. JOHNSTON.

"The complex cyanides of molybdenum." By W. R. BUCKNALL and W. WARDLAW.

"The parachor and chemical constitution. Part VI. Some cases of supposed ring-chain tautomerism." By F. B. GARNER and S. SUGDEN.

"The polymerides of some diaryl-ψ-thiohydantoins and of some 2 : 4-diaryl-tetrahydro-1 : 2 : 4-thiodiazole derivatives." By R. F. HUNTER and H. MORLAND.

"Studies of valency. Part VIII. Extinction coefficients and molecular conductivities of Vernon's isomeric α- and β-dimethyltelluronium salts. The molecular structure of quadrivalent tellurium compounds." By T. M. LOWRY, R. R. GOLDSTEIN, and F. L. GILBERT.

"The isomerism of the oximes. Part XXXIII. The oximes of opianic acid and of phthalic anhydride." By O. L. BRADY, L. C. BAKER, R. F. GOLDSTEIN, and S. HARRIS.

"The colouring matters of Carajura." By E. CHAPMAN, A. G. PERKIN, and R. ROBINSON.

"Trypanocidal action and chemical constitution. Part VII. *s*-Carbamides and arylamines of naphthylamine di- and tri-sulphonic acids with some observations on the mesomorphic state." By I. E. BALABAN and H. KING.

"The preparation of mono- and di-nitro-derivatives of benzil." By F. D. CHATTAWAY and E. A. COULSON.

"Studies in colour and constitution. Part II. Further group influences on the colours of azo-dyes." By H. H. HODGSON and F. W. HANDLEY.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

(a) *From Lady Ramsay.*

ARRHENIUS, SVANTE. Theorien der Chemie. Translated by ALEXIS FINKELSTEIN. Leipzig 1906. pp. vii + 177. ill.

—— Das Werden der Welten. Translated by L. BAMBERGER. Leipzig 1907. pp. vi + 208. ill.

LE CHATELIER, HENRY. La silice et les silicates. Paris 1914. pp. iv + 574. ill.

MENDELÉEFF, DMITRI [IVANOVICH]. Grundlagen der Chemie. Translated by L. JAWEIN and A. THILLOT. St. Petersburg 1891. pp. iv + 1126. ill.

MOISSAN, HENRI. Recherches sur l'isolment du fluor. Paris 1887.

—— Le four électrique. Paris 1897. pp. viii + 386. ill.

RIGHI, AUGUSTO. La moderna teoria dei fenomeni fisici (radio-attività, ioni, elettroni). 3rd edition. Bologna 1907. pp. xii + 290. ill.

(b) *From Mr. Arnold Stevenson.*

CLIFTON, E., and GRIMAUX, A. Nouveau dictionnaire Anglais-Français et Français-Anglais. New edition. By J. MCLAUGHLIN. Paris [1914]—1923. pp. xxiv + 1237, xviii + 1341. (*Reference.*)

HOARE, ALFRED. An Italian dictionary. Cambridge 1925. pp. xxxii + 906. (*Reference.*)

KRAMERS' Engelsch woordenboek: Engelsch-Nederlandsch en Nederlandsch-Engelsch. 10th edition. By F. P. H. PRICK VAN WELY. Gouda 1926. pp. viii + 1260. ill. (*Reference.*)

ROSHDESTVENSKY, A. P., and SHAPIRO, A. M. Hill's modern pronouncing dictionary of the English and Russian languages. 2 vols. London 1919. pp. vi + 532, viii + 682. (*Reference.*)

(c) *Miscellaneous.*

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trizität und Magnetismus. Edited by WILHELM WESTPHAL. Berlin 1927. pp. ix + 801. ill. *M.* 68.40. (*Recd.* 2/9/27.)

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REMY, HEINRICH. Die elektrolytische Wasserüberführung und ihre Bedeutung für die Theorie der wässerigen Lösungen. (Fortschritte der Chemie, Physik und physikalischen Chemie, Vol. XIX.) Berlin 1927.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, November 3rd, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death on October 10th, of Mr. A. C. P. Lunn, who was elected a Fellow on May 4th, 1922.

It was announced that Professor C. S. Gibson, Dr. J. T. Hewitt, Professor G. T. Morgan, and Professor J. F. Thorpe had been reappointed by the Council to represent the Society on the Bureau of Chemical Abstracts for the year 1927—1928, and that Professor A. J. Allmand, Professor F. G. Donnan, and Dr. T. Slater Price would represent the Society on the Editorial Board of the "Journal of Physical Chemistry," together with Dr. E. K. Rideal, the representative of the Faraday Society.

The following were formally admitted Fellows of the Chemical Society: G. E. Thompson, J. Muir Smith, R. A. B. Tapley, W. L. Lee-Smith, J. Wilson, and L. V. D. Scorah.

Certificates were read for the first time in favour of:

William Ernest Cooper, 105, Park Road, Warley Woods, Birmingham.
Eustace Nevill Eccott, B.Sc., A.R.C.S., Crofton Acre, Orpington.
Barnett Levin, B.Sc., 64, Pooles Park, N. 4.
Ronald Henry Linsell, B.Sc., Bethary House School, Goudhurst.
Moolraj Mehrotra, M.Sc., 112, Gower Street, W.C. 1.
Thomas Mitchell, B.Sc., A.R.C.S., 2, Tufton Street, Silsden, Keighley.
William Emrys Pride, B.Sc., A.R.C.S., Imperial College Hostel, S. Kensington, S.W. 7.
Ralph David Satchell, B.Sc., A.R.C.S., 26, Wilson Street, S.W. 11.
Arthur Harold Stevens, B.Sc., Tower House, Wokingham Road, Reading.
Horatio Todd, Bromleigh, Sandown Road, Knock, Belfast.
Frank Louis Warren, B.Sc., A.R.C.S., 5, Maitland Park Villas, Hampstead, N.W. 3.
Marjorie Jennet Wilson-Smith, B.Sc., 90, Queen Alexandra Mansions, Judd Street, W.C. 1.

Dr. J. L. Simonsen and Dr. C. R. Young were appointed Scrutators, and a ballot for the election of Sir Joseph John Thomson, O.M., F.R.S., Master of Trinity College, Cambridge, as an Honorary Fellow was held. Sir J. J. Thomson was subsequently declared duly elected.

The following papers were read :

"The complex salts of nickel with various aliphatic diamines." By F. G. MANN.

"The mechanism of the formation of citric and oxalic acids from sugars by *Aspergillus niger*." By T. K. WALKER, V. SUBRAMANIAM, and F. CHALLENGER.

"The complex cyanides of molybdenum." By W. R. BUCKNALL and W. WARDLAW.

"The parachor and chemical constitution. Part VI. Some cases of supposed ring-chain tautomerism." By F. B. GARNER and S. SUGDEN.

"The colouring matters of *Carajura*." By E. CHAPMAN, A. G. PERKIN, and R. ROBINSON.

Ordinary Scientific Meeting, Thursday, November 17th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc. F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death on March 9th, of Professor Albert William Smith, who was elected a Fellow on May 4th, 1922.

Certificates were read for the first time in favour of :

Jacob Davis Cohen, B.Sc., A.C.G.F.C., 24, Alconbury Road, Clapton, E. 5.
Geoffrey William Fenton, B.Sc., 7, St. John's Avenue, Newcome, Huddersfield.
James Flint, M.C., 82, Sunny Gardens, Hendon, N.W. 4.
Charles Frederick Goodeve, M.Sc., University College Hall, Ealing, W. 5.
Marion Gosset, B.Sc., A.R.C.S., 17, Queen Anne's Grove, Bedford Park, W. 4.
Leslie George Groves, B.Sc., 22, Chadway, Chadwell Heath, Essex.
Herbert Charles Gull, B.Sc., 26, Twyford Road, Ilford.
Donald Holroyde Hey, B.Sc., 14, Grosvenor Road, Sketty, Swansea.
Theodora Mary Holmes, B.Sc., A.R.C.S., 24, Clifton Gardens, W. 9.
Robert Gilbert James, B.Sc., A.I.C., 25, Staplehall Road, Northfield, Birmingham.
Alfred William Leonard, B.Sc., 72, Hatherley Gardens, East Ham, E. 6.
Arthur Bertram Edmund Lovett, B.Sc., 4, Prior Street, Greenwich, S.E. 10.
Alfred Pollard, B.Sc., Hulme Hall, Victoria Park, Manchester.
John Taylor, B.Sc., 120, Hurlingham Road, Fulham, S.W. 6.
David Matthew Williams, B.Sc., Ph.D., Cranbrooke, Bridge Street, Aberystwyth.

The following papers were read :

"Differential potentiometric titration. Part I. Simple method." By B. CAVANAGH.

"Differential potentiometric titration. Part II. Refined method." By B. CAVANAGH.

"A general method for the preparation of carbocyanine dyes." By F. M. HAMER.

"A comparison of analogous organic compounds of phosphorus and arsenic." By C. S. GIBSON and J. D. A. JOHNSON.

"Derivatives of methyl 2 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylate." By C. S. GIBSON, K. V. HARIHARAN, and J. L. SIMONSEN.

IMPORTANT NOTICE.

Ordinary Scientific Meeting, December 15th, 1927.

It has been decided to abandon the Ordinary Scientific Meeting arranged for December 15th, 1927, in view of the Jubilee Dinner of the Institute of Chemistry being held that evening.

List of Papers, or Abstracts thereof, received between October 20th and November 17th, 1927. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The ternary systems : copper acetate–acetic acid–water and lead acetate–acetic acid–water at 25°." By K. SANDVED.

"A method of estimating traces of zinc in solution (other metals being absent)." By R. PIRRET.

"The photochemical decomposition of nitrous oxide and nitric oxide." By J. Y. MACDONALD.

"Investigation of the constitution of glycerides in natural fats. A preliminary outline of two new methods." By T. P. HILDITCH and C. H. LEA.

"The interaction of bromine with acetic anhydride. Part III. Arrest of the reaction. A comparison with the bromination of acetone." By H. B. WATSON.

"Some observations on the chlorination products of ββ′-dichlorodiethyl sulphide." By S. A. MUMFORD and J. W. C. PHILLIPS.

"The oxide-ring structure of normal and γ-derivatives of mannose. Preparation and oxidation of derivatives of γ-mannonolactone and δ-mannonolactone." By E. H. GOODYEAR and W. N. HAWORTH.

"The effect of the constitution of a chloroamine on its hydrolysis constant." By F. G. SOPER and G. F. SMITH.

"The use of hydrogen peroxide in iodine and other substitutions." By J. E. MARSH.

"The reactivity of the double bond in coumarins and related αβ-unsaturated carbonyl compounds. Part I. Addition of cyanacetamide to coumarins." By T. R. SESHADRI.

"The nature of the alternating effect in carbon chains. Part XXII. An attempt further to define the probable mechanism of orientation in aromatic substitution." By C. K. INGOLD and F. R. SHAW.

"Nitration of diacetyl-*o*-phenylenediamine." By M. A. PHILLIPS.

"The formation of 2-methylbenziminazoles." By M. A. PHILLIPS.

"The influence of glass upon the vapour pressure." By J. RINSE.

"Action of cuprous hydride on diazonium salts—a combined Sandmeyer–Gattermann reaction." By P. NEOGI and A. K. MITRA.

"The inflammation of mixtures of (*a*) carbon monoxide and air, (*b*) hydrogen and air in a closed spherical vessel." By G. B. MAXWELL and R. V. WHEELER.

"On the heat of adsorption of oxygen on charcoal." By A. F. H. WARD and E. K. RIDEAL.

"The laws of aromatic substitution. Part VI. The constitution and substitution of phenylnitromethane and some derivatives." By B. FLÜRSCHEIM and E. L. HOLMES.

"The laws of aromatic substitution. Part VII. A quantitative method for rapid determinations of isomeric nitro-derivatives of laterally substituted toluenes." By B. FLÜRSCHEIM and E. L. HOLMES.

"Researches in residual affinity and co-ordination. Part XXX. Complex ethylenethiocarbamide salts of univalent and bivalent metals." By G. T. MORGAN and F. H. BURSTALL.

"Optical activity and the polarity of substituent groups. Part VII. *sec.*-β-Octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids." By H. G. RULE, W. HAY, A. H. NUMBERS, and T. R. PATERSON.

"A cyclic semipinacolin." By J. W. COOK.

"Activation of extended conjugated systems. A reply." By J. W. BAKER and I. S. WILSON.

"On an auto-poisoning phenomenon shown by catalytically active copper at moderate temperatures." By F. H. CONSTABLE.

"The condensation of glyoxalines with formaldehyde." By R. GRINDLEY and F. L. PYMAN.

"Glyoxaline-4(5)-formaldehyde." By W. HUBBALL and F. L. PYMAN.

"Orientation effects in the diphenyl series. Part V. The independence of the two nuclei in diphenyl compounds as evidenced by substitution and reactivity effects." By R. J. W. LE FÈVRE and E. E. TURNER.

"Action of Beckmann's chromic acid mixture on some monocyclic terpenes." By T. A. HENRY and H. PAGET.

"Applications of thallium compounds in organic chemistry. Part IV. Thallium compounds of polyhydroxy-compounds." By R. C. MENZIES and M. E. KIESER.

"Density and refractivity of dilute manganese salt solutions." By A. N. CAMPBELL.

"Studies of dynamic isomerism. Part XXVI. Consecutive changes in the mutarotation of galactose." By G. F. SMITH and T. M. LOWRY.

"Triazole compounds. Part II. Methylation of some 1-hydroxy-1 : 2 : 3-benztriazoles." By O. L. BRADY and C. V. REYNOLDS.

"Campnospermonol, a ketonic phenol from *Campnospermum brevipetiolatum*." By T. G. H. JONES and F. B. SMITH.

"Cyclic organo-metallic compounds. Part IV. Tellurylium compounds (*continued*)." By H. D. K. DREW.

"Cyclic organo-metallic compounds. Part V. Phenoxselenine and phenoxthionine from phenoxtellurine. Selenylium and thionylium compounds." By H. D. K. DREW.

"Stereoisomerism of disulphoxides and related substances. Part II. Derivatives of 1 : 4-dithian." By E. V. BELL and G. M. BENNETT.

"The velocity coefficient for bimolecular reactions in solution." By R. G. W. NORRISH and F. F. P. SMITH.

"The constitution of the disaccharides. Part XVIII. Maltose and melibiose." By W. N. HAWORTH, J. V. LOACH, and C. W. LONG.

"The hydrogen-ion concentration of aqueous iodine solutions." By H. M. DAWSON.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, DECEMBER 1st, 1927.

BIRKS, STANLEY, The Limes, High View Av., Grays, Essex. British. Science Master. 2nd Class Honours School Natural Science (Chemistry),

Oxford. Teacher of Chemistry at Palmer's School, Grays, Essex (Sept. 1922). (*Signed by*) H. J. George, D. L. Chapman, M. P. Applebey.

BLYTHE, GEORGE EDWARD KEVIN, "Ael-y-Bryn," 20, Pantygwydr Road, Uplands, Swansea. British. County Lecturer in Electrotechnics to the Glamorgan County Council. Doctor of Philosophy. B.Sc. Lecturer in Chemistry and Scholar Leeds University. Jarrow-on-Tyne Secondary School Honours Diploma, City and Guilds. Fellow Royal Astronomical Society. Fellow of Geological Society. Member Royal Institution of Great Britain. Laureate French Academy of Science. Fellow Société Astronomique de France. Associate American Institute of Electrical Engineers. Graduate Institution of Electrical Engineers (London). Graduate Institution of Structural Engineers (London). "Mineral Oil—Petroleum," "Powdered Fuel," "The Corrosion of Metals," Durham University, February, 1925. (*Signed by*) Julius B. Cohen, Edward John Jones, Arthur M. O'Brien.

CLAY, CHARLES NIGHTINGALE, 81, Cromwell Road, London, S.W. 7. British. Industrial Chemist. B.Sc. (1st Class Honours in Chemistry at University College, London). A.I.C. Wish to receive publications of the Society and to attend the meetings. (*Signed by*) F. A. Freeth, L. W. Codd, F. M. Irvine.

COOPER, WILLIAM ERNEST, 105, Park Rd., Warley Woods, Birmingham. British. Assistant Works Chemist. Five years at Messrs. Guest, Keen & Nettlefolds, Ltd., Birmingham. Studied one year at Birmingham University. Studied four years at Birmingham Municipal Technical School. Student of Inst. of Chemistry. Six years' works technical experience. (*Signed by*) J. Newton Friend, J. Cooper Duff, Wm. Wardlaw.

COPPOCK, PHILIP DALTON, 50, Albany Rd., Victoria Park, Manchester. English. Technical and Research Chemist. B.Sc. Hons. Chem. (Manchester). M.Sc.Tech. (Manchester). Assistant to T. R. Hodgson, M.A., F.I.C., Public Analyst for Blackpool, Wallasey, etc., Jan.–May, 1926, and July, 1927 to date. Evening Demonstrator in Chemistry and Bacteriology of Foodstuffs. Manchester College of Technology, Sept., 1926 to date. (*Signed by*) T. K. Walker, John K. Wood, T. R. Hodgson.

CORDER, BENJAMIN JOHN (Rev.), The Rectory, Radnage, High Wycombe. British. Clerk in Holy Orders. B.A. (Cantab.). Work on Electrochemistry. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox.

ECCOTT, EUSTACE NEVILL, Crofton Acre, Orpington, Kent. British. Student (Chemistry). B.Sc. (2nd Class Honours, London). A.R.C.S. (*Signed by*) H. B. Baker, M. A. Whiteley, G. A. R. Kon.

ENGLAND, HERBERT, 22, Queen's Road, Harrogate, Yorkshire. British. Chemist Director (Taylor's Drug Co., Ltd.). Chemist and Druggist, Edinburgh. In control of the Company's Laboratory and Dispensaries. I desire to keep abreast with modern scientific literature and development. (*Signed by*) J. Langford Moore, John Rennie, H. Roberts.

FINÁLY, STEPHEN DE, Budapest, Hungary, IX. Lónyay-utra 41. Hungarian. Analytical Chemist of the Royal Hungarian Geological Survey, Budapest. Diploma of Chemical Engineering issued by the Royal Hungarian "Joseph" University of Technical Sciences, Budapest. (*Signed by*) Thos. J. Cheater, William T. Burgess, R. Sutcliffe.

FITZGERALD, ROBERT RAILTON, 68, Bath Row, Birmingham. British Head Brewer. To keep in touch with the latest developments in Biological Chemistry. (*Signed by*) S. H. Green, William Duncan, E. C. Bennison.

GERRY, HORACE LEONARD, Lyndall, Queen's Park, Chester. British. Pharmacist. Member of the Pharmaceutical Society of Great Britain. Has worked for 12½ years on the Chemistry of Soils and Soil Sterilisation for

Horticultural purposes. Is desirous of receiving the Society's Publications and of attending its meetings. (*Signed by*) John Welsh, W. H. Saunders, George Dalrymple.

GLOVER, THOMAS JOSEPH, 40, Curzon St., South Circular Road, Dublin. Irish. Lecturer in Chemistry, Birmingham University. M.Sc. and Ph.D., National University, Ireland. Papers, with Prof. Hugh Ryan, on "Nitro-derivatives of Diphenylamine" (*Proceedings of the Royal Irish Academy*) and, with Prof. G. T. Morgan, on the "Orthochlorodinitrotoluenes" *J.C.S.*, 1921, 1700; 1924, 1597. (*Signed by*) Wm. Wardlaw, W. J. Hickinbottom, H. D. K. Drew.

HARINGTON, CHARLES ROBERT, 2, The Greenway, Gerrards Cross, Bucks. British. Lecturer in Pathological Chemistry, University College Hospital Medical School, London. M.A. (Cantab.), Ph.D. (Edin.). Papers on chemical subjects in the *Biochemical Journal* (including "Constitution and Synthesis of Thyroxine"). (*Signed by*) George Barger, Ellen Stedman, C. P. Stewart.

HAYMAN, EDGAR ALBERT, "Cranleigh," 100, Doyle Gardens, Harlesden, N.W. 10. British. Chemist and Druggist. Member of Pharmaceutical Society. Desirous of attending meetings and to receive the publications of the Society. (*Signed by*) Frank B. Arnold, Percy Barrs, Alfred J. Lennane.

HUSSEY, HERBERT RICHARD, 31, Thornbury Avenue, Southampton. British. Managing Director of Randall & Wilson, Ltd., Manufacturing Chemists, Southampton. My object in being a Fellow is to attend the meetings; also to receive the *Journal* and other publications. (*Signed by*) Fred. W. Fletcher, D. R. Boyd, Herbert J. Hodges.

INGRAM, ALBERT WILLIAM KEMP, "St. Stephens," 261, High Street, Sheerness, Kent. British. B.A. Student at Emmanual College, Camb. Entering Teaching Profession as Chemistry Master. B.A. (Cantab.). Natural Science Tripos, Part I. Reading for Camb. Univ. Diploma in Education, with special endorsement in Science. (*Signed by*) R. G. W. Norrish, F. W. Dootson, C. R. Ward.

JONES, JOHN WILLIAM THOMAS, 112, Gaskarth Road, London, S.W. 12. British. Research Student. A.R.C.S. (*Signed by*) H. B. Baker, Jocelyn Thorpe, M. A. Whiteley, G. A. R. Kon, Philip C. Bull, R. F. Hunter.

KERR, ROBERT NAPIER, 22, St. Bernard's Crescent, Edinburgh. British. University Assistant. B.Sc., Ph.D. (Edinburgh). Assistant in Chemistry, Edinburgh University, 1926–27. Carnegie Research Scholar, 1925–26. *J.C.S.*, 1926, 2796; *Phil. Mag.*, 1927, 330. (*Signed by*) James Walker, H. Gordon Rule, Ernest B. Ludlam.

KING, REGINALD BENJAMIN, Lemsford, 52, Mostyn Road, Merton Park, Surrey. British. Student. B.Sc., London (Hons. Chem.), 1925. Two years' research to 1927, King's College, London. A.I.C. (*Signed by*) Samuel Smiles, A. J. Allmand, E. W. McClelland.

KITASATO, ZENJIRO, Chemical Department, The University, Manchester. Japanese. D.Sc., University of Tokyo. Have been engaged in research-work for eight years in Japan. Am now engaged at the University of Manchester under Professor R. Robinson, F.R.S. "Beiträge zur Kenntnis der Isochinolin-Alkaloide," *Acta Phytochimica* (*Japan*), Vol. III, No. 2. (*Signed by*) Robert Robinson, Arthur Lapworth, H. Raymond Ing, Ernest Wignall.

KNY-JONES, FREDERIC GORONWY, 1, Linley Road, Bruce Grove, London, N. 17. British. Training for Secondary School teaching. B.Sc. (Second Class Honours Chemistry). (*Signed by*) J. R. Partington, E. E. Turner, F. E. King.

LAWRENCE, CYRIL DUNN, 46, Juer St., Park Rd., Battersea, S.W. 11.

British. Research Student at the Imperial College of Science and Technology B.Sc., London (Honours, Chemistry). (*Signed by*) E. H. Farmer, G. A. R. Kon, Arnold Stevenson.

LEVIN, BARNETT, 64, Pooles Park, Finsbury Park, N. 4. British. Organic Research Student. B.Sc., London, 1926. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, Arnold Stevenson.

LINSELL, RONALD HENRY, Bethany House School, Goudhurst, Kent. English. Science and Mathematics Master. B.Sc., London (Hons. Chemistry). As a teacher of Chemistry, I wish to keep up to date with present research, and prepare to do research of my own for further qualifications. (*Signed by*) J. R. Partington, E. E. Turner, A. Brewin.

McBRIDE, JOHN, Uzina Sinimbri, São Miguel de Campos, Alagôas, Brazil. British. Analytical Chemist. Seven years in Laboratory of Messrs. John Walker & Co., Sugar Refiners, Greenock; 3½ years in laboratories of C.U.C.S., Pernambuco, Brazil; now head chemist to this company. (*Signed by*) Angus Smith, John Wm. Biggart, William M. Cumming.

MACDONALD, JAMES YOUNGER, 17, Learmonth Gardens, Edinburgh. British. Lecturer in Chemistry, University of St. Andrews (from August, 1927). B.A. (Nat. Sci., Oxon.). Three years as research student. *J.C.S.*, 1925, **127**, 2764. (*Signed by*) F. G. Donnan W. E. Garner, Henry Terrey.

McNEIL, JAMES ERIC, "Claremont," Lake Road East, Cardiff. British. Colliery Chemist. At present Assistant to Tredegar Iron & Coal Co., Tredegar, Mon. B.Sc. (3rd Class Honours in Chemistry) in University of Wales. Long vacations of 1924 and 1925 spent in laboratory of Messrs. Treharne & Duncan, Cardiff. (*Signed by*) J. H. Duncan, A. A. Read, E. P. Perman.

MEHROTRA, MOOLRAJ, Chemistry Department, University of Allahabad, Allahabad. Indian. Demonstrator in Chemistry, University of Allahabad. B.Sc. and M.Sc. of the University of Allahabad. I have been on the staff of the University of Allahabad for four years and have contributed eight papers on Colloid Chemistry. Two of them are in the press, and the following six have been published: 1. "Adsorption von Saüren, Basen und Satzen, etc.," M. R. Mehrotra and N. R. Dhar (*Zeit. Anorg.*, Chemie Band 155). 2. "Die Stabilität Kolloidaler Lösungen, Pt. II," K. C. Sen and M. R. Mehrotra (*Zeit. Anorg. Chemie*, Band 142). 3. "Peptisation of Metallic Hydroxides in Presence of Sugars," M. R. Mehrotra and K. C. Sen (*J. Ind. Chem. Soc.*, 1927, **4**, 117). 4. "Simultaneous Adsorption of Ions from Solution, Pt. I, etc.," Moolraj Mehrotra and Kshitish Chandra Sen (*J. Ind. Chem. Soc.*, 1926, **3**, 297). 5. "Studies in Adsorption, Pt. XV," M. R. Mehrotra and N. R. Dhar (*J. Phys. Chem.*, 1926, **30**, 1185). 6. "Die peptisation von Eisen und Chromhydroxyd, etc.," M. R. Mehrotra and K. C. Sen (*Koll. Zeit.*, 1927, **42**, 35). (*Signed by*) F. G. Donnan, S. Barratt, Henry Terrey.

MEREDITH, DAVID OWEN, P.O. Box AA-B, Hobart, Tasmania. Australian. General Superintendent, Electrolytic Zinc Co. of Australasia, Ltd. In charge of Electrolytic Zinc Co. of Australasia's operations at Risdon, Tasmania, formerly as Deputy General Manager and now as General Superintendent. These works cover the electrolysis of zinc and cadmium, also production of sulphuric acid, nitric acid, and superphosphate. Member Australasian Institute of Mining and Metallurgy. Member American Institute of Mining and Metallurgical Engineers. Member Institution of Engineers (Australia). Member American Chemical Society. (*Signed by*) D. Avery, Gilbert Rigg, D. Orme Masson.

MILLARD, ARTHUR HEREWARD, 8, Westhall Rd., Park Lane, Bath. British. Lecturer at the Bath and West of England College of Chemistry and Pharmacy. Qualifying Examination of Pharmaceutical Soc., Jan. 5, 1925. Pharmaceuti-

cal Chemist Diploma, July 22, 1925. Three years student and 6 years as Demonstrator and Lecturer in Pharmaceutical Chemistry at The Bath and West of England College of Chemistry and Pharmacy. Desirous of keeping in touch with chemical research. (*Signed by*) David J. Williams, Arthur Marsden, P. J. Thompson.

MITCHELL, THOMAS, 2, Tufton St., Silsden, nr. Keighley, Yorks. British. Research Student. B.Sc., London (Hons.). A.R.C.S. (Hons.). (*Signed by*) G. A. R. Kon, W. E. Hugh, H. L. Riley.

MURAKAMI, SHINZO, Chemical Department, The University, Manchester. Japanese. Instructor in the Pharmaceutical College, Osaka (Japan). Have been engaged in research work for 10 years in Japan and now in the University of Manchester under Prof. R. Robinson. "On New Constituents of the Ava root" (*Journ. Pharm. Soc., Japan*, 1916, 1918). "On the Essential Oil of *Houttuynia cordata*, Thumb. (*ibid.*, in the press). (*Signed by*) Robert Robinson, Arthur Lapworth, H. Raymond Ing, Ernest Wignall.

NODZU, RYUZABURO, Chemical Department, The University, Manchester. Japanese. Assistant Professor of Organic Chemistry, Kyoto Imperial University, Japan. D.Sc., Kyoto Imperial University. Have engaged in research work under Prof. S. Komatsu. Joint author of the following papers: "Reaction between Aniline and Chloroacetic Acid," *Mem. Coll. Sci. Kyoto*, 1922, VI, 73; "Studies on Catalytic Action, I," *loc. cit.*, 1923, VI, 177; "On the Synthesis of Phosphoric Acid Esters, II," *loc. cit.*, 1924, VII, 377; "On the Chemistry of Japanese Plants, VII," *loc. cit.*, 1925, VIII, 223. Author of the following paper: "On the Synthesis of the Phosphoric Acid Esters, III," *J. Biochem.*, 1926, VI, 31. At present working under Prof. R. Robinson, F.R.S., at University of Manchester. (*Signed by*) Robert Robinson, Arthur Lapworth, Reginald C. Fawcett, H. Raymond Ing, Ernest Wignall.

OOMMEN, MARIAM PUTHENPARAMPIL, 59, Tregunter Road, West Brompton, London, S.W. 10. Indian. Lecturer in Chemistry, Women's Christian College, Madras, S. India. Now Research Student at Royal College of Science, London. B.A. (Hons.) Chemistry (Madras University), 1924. (*Signed by*) James C. Philip, M. A. Whiteley, B. B. Dey, Jocelyn Thorpe.

OSWALD, WILLIAM ALEXANDER HUGH, White Knights, St. George's Hill, Weybridge, Surrey. British. Technical Department, Anglo-American Oil Co., Ltd. B.A., Cambridge University, 1st Class Inorganic and Organic Chemistry, Physics, Industrial, Commercial, and Applied Chemistry. I have spent some time in the Imperial Oil Co. Refinery in Sarnia, Canada, chiefly in connection with "cracking" and vacuum distillation; also some months in the Research Laboratories of the Standard Oil Co. (N.J.) in connection with testing chemical substances for their "anti-knocking" properties when added to petrol; research on lubricating oils, fuel oils, and Diesel oils; vacuum distillation and vapour-phase "cracking." I spent a month in Dr. F. H. Garner's Laboratory at Fawley. (*Signed by*) C. I. Kelly, C. Chilvers, Walter A. Woodward.

PAVION, HARRY, 4, Brideoak St., Cheetham, Manchester. British. Chemist and Representative at Messrs. N. Taylor & Co., 105, Hulme Hall Lane, Miles Platting, Manchester. Associate of Pharmaceutical Society of Gt. Britain (1906–1912). Registered Medical Student at Victoria University, Manchester (1914–1919). Senior Sergt. Dispenser, R.A.M.C. (T.F.) at home and abroad, Field Ambulance and General Hospital. Late Managing Director to Messrs. Rubwel Co., Ltd., Manchester, Manufacturing Chemists, etc. (*Signed by*) H. Berry, Fred Fairbrother, J. E. Myers.

PERRINS, GORDON, Chemical Laboratory, Royal Infirmary, Edinburgh.

British. Chief Pharmacist to Royal Infirmary, Edinburgh. Manufacturing and Analytical Chemist, Teacher of Pharmacy. Pharmaceutical Chemist and Teacher of Chemistry. Occasional contributor to *Pharmaceutical Journal* on educational matters, in which I am particularly interested; late Secretary to Ipswich Pharmaceutical Association; Lecturer to Edinburgh Chemists' Association. (*Signed by*) Arthur W. Mann, J. F. Ward, J. Macvie Hill, D. Hughes, William Mair, H. P. Wilson.

PRASAD, MATA, Royal Institute of Science, Bombay, India. Indian. Professor in Inorganic and Physical Chemistry, Royal Institute of Science, Bombay (India). D.Sc. of Benares Hindu University. Published a number of papers in *Koll. Zeit.*, *Jour. Phys. Chem.*, *Zeit. physikal. Chem.*, and *Jour. Ind. Chem. Soc.* Working at present at Davy-Faraday Laboratory on crystal structure. Member of the Royal Institution. Published no paper in *J.C.S.* so far. (*Signed by*) W. E. Garner, Henry Terrey, L. F. Gilbert.

PRIDE, WILLIAM EMRYS, Imperial College Hostel, South Kensington, S.W. 7. British. Research Student. A.R.C.Sc., B.Sc. (Imperial College of Science and Tech., London). (*Signed by*) Jocelyn Thorpe, M. A. Whiteley, James C. Philip, R. F. Hunter.

RAO, BIJOOR SANJIVA, Bangalore. Hindu. Assistant Chemist, Department of Organic Chemistry, Indian Institute of Science, Hebbal, Bangalore. B.A. (Madras); Associate Indian Institute of Science; some time Assistant Lecturer, Central College, Bangalore; then Assistant Chemist, Mysore Govt. Sandalwood Oil Factory; from 1921 Assistant Chemist, Indian Institute of Science. Published following joint papers in the *Jour. Ind. Inst. Sci.*, "West Australian Sandalwood Oil," 1922, V, pt. 12; "Kochi Grass Oil," 1925, VIIIA, pt. 2; "Essential Oil of *Cyperus Rotundus*," 1925, VIIIA, pt. 4; "Notes on Indian Essential Oils," 1925, VIIIA, pt. 10; "Occurrence of Sylvestrene," 1925, VIIIA, pt. 14; "Essential Oils from *Kaempferia galanga*, *Curcuma aromatica*, and *Erythroxylon monogynum*," 1926, IXA, pt. 6. "The Occurrence of Sylvestrene," *J.C.S.*, 1925, **127**, 2494. (*Signed by*) J. L. Simonsen, Roland V. Norris, M. O. Forster.

RAYMOND, WALTER DESMOND, Chemical Laboratory, Baghdad. British by birth. Assistant Chemical Examiner to the Govt. of Iraq. Formerly student at Sir John Cass Technical Institute, Aldgate, E. Formerly Assistant to R. H. Ellis, Esq., F.I.C., F.C.S., at Olympia Oil and Cake Co., Ltd., Selby. B.Sc., London University. Lecturer in Chemistry to the Iraq School of Pharmacy. (*Signed by*) E. de Barry Barnett, J. W. Cook, Henry J. S. Sand.

RHYS-JONES, DAVID CLARENCE, 10, Berkley Av., Levershulme, Manchester. British. Research Student, Manchester University. B.Sc. (Wales). (*Signed by*) Frank Lee Pyman, Frederick A. Mason, John K. Wood, O. Rhys Howell.

ROBINSON, ALBERT ERNEST, 14, Brentwood Terrace, Armley, Leeds. English. Works Colour Chemist. Now Departmental Manager at Messrs. Wood & Bedford, Branch of the Yorkshire Dyeware & Chemical Co., Ltd. Matriculation, Northern Universities, 1917 (private study); Final Certificates in Wool and Cotton Dyeing, London Institute; Group Certificate of Leeds Technical College; Two years' Leather Manufacture and Analysis at University of Leeds; Eleven years as Works Colour Chemist. I wish to keep in touch with Chemical Research. (*Signed by*) Chas. S. Bedford, Ralph C. Storey, C. W. H. Story.

SATCHELL, RALPH DAVID, 26, Wilson St., London, S.W. 11. British. Student, Organic Research at Imperial College of Science and Technology. A.R.C.S., B.Sc. (Hons.). (*Signed by*) G. A. R. Kon, W. E. Hugh, J. C. Bardhan.

SCOTT, WILLIAM DALLAS, Eldercroft, Cassio Rd., Watford, Herts. British. Student. Diploma of the Associateship of the Royal College of Science and proceeding to higher degrees. (*Signed by*) G. A. R. Kon, Arnold Stevenson, M. A. Whiteley.

SOMERVILLE, IAN CAMPBELL, 319, Ryers Avenue, Cheltenham, Pa., U.S.A. British. Research Chemist. Graduated from Edinburgh University, B.Sc., 1st Class Hons. Chem., 1923. Assistant in Physical Chemistry in Edinburgh University, 1923–25. Thesis accepted for Ph.D., July, 1926. Jointly with Dr. J. D. M. Ross, *J.C.S.*, 1926, 2770. "Melting-point Curves of Optical Isomerides in the Camphor Series." (*Signed by*) James Walker, John D. M. Ross, Alex. McKenzie.

STEVENS, ARTHUR HAROLD, Tower House, Wokingham Road, Reading (Berks.). British. Chartered Patent Agent. B.Sc. (in Chemistry, Physics, and Maths. at London University). Passed Final Exam. for Assoc. Mem. Inst. C.E., taking Metallurgy as one subject. Have obtained patents on many chemical inventions for clients, including 155092 (water softening); 120381 (arsenical compounds); 249172 (rubber substitutes); 249526 (azo-dyes); 217391 (lead refining); 273017 (pigments); 275328 (yeast). (*Signed by*) H. Harris, S. Judd Lewis, J. N. Goldsmith.

TODD, HORATIO, Bromleigh, Sandown Road, Knock, Belfast. British. Pharmaceutical Chemist. President Pharmaceutical Soc., Northern Ireland. Licentiate and Member Pharmaceutical Society of Ireland. Member, ex-Committee, British Pharmaceutical Conference. Ex-President North Irish Pharmacists Assoc. (2 years). Desirous of admission to the Society in order to keep in touch with current advances in chemistry, particularly in relation to pharmacy and medicine. No published papers in Journals of Chemistry. (*Signed by*) Henry Wren, Theo. Harper, Chas. J. Still, William Macartney.

WALTON, ROBERT, The Mill House, Langford, Malden, Essex. British. Chemist to Southend Waterworks Co. Student of Chemistry desirous of using the library and receiving the Journal. (*Signed by*) P. C. L. Thorne, E. de Barry Barnett, J. W. Cook.

WARREN, FRANK LOUIS, 5, Maitland Park Villas, Haverstock Hill, Hampstead, N.W. 3. British. Research Student. B.Sc. (Imperial College of Science and Technology, London), A.R.C.S. (*Signed by*) Jocelyn Thorpe, M. A. Whiteley, James C. Philip.

WILSON-SMITH, MARJORIE JENNET, 90, Queen Alexandra Mansions, Judd Street, London, W.C. 1. British. Research Student, Organic Chemistry Dept., Imperial College of Science and Technology. B.Sc. (London), Royal Holloway College, Englefield Green, Surrey. 1. Lindley Studentship in Physiology, London University, 1922–23. 2. Demonstrator in Chemistry, London School of Medicine for Women, 1921–22 and 1923–25. (*Signed by*) M. A. Whiteley, Jocelyn Thorpe, E. H. Farmer, G. A. R. Kon.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

LEECH, PAUL NICHOLAS, American Medical Association, 535, N. Dearborn St., Chicago, Ill., U.S.A. Born in U.S.A. Director Chemical Laboratory, Amer. Med. Assoc. A.B. Miami Univ.; Sc.M. Univ. of Chicago; Ph.D. Univ. of Chicago. Various articles in Chemical and Medical Literature since 1913. Articles have been published in *J. Am. Chem. Soc.* (with J. Stieglitz), *Industrial and Engineering Chemistry*, *J. Am. Pharm. Assoc.*, and *J. Am. Med. Assoc.* Have also written many unsigned articles and editorials principally in *J. Am. Med. Assoc.* Chairman Chicago Section of the American

Chem. Soc., 1926–27. Assoc. Fellow American Med. Assoc. (*Signed by*) A. H. Clark.

RUFF, OTTO, Dr.phil., Dr.Ing.Eh., Breslau (Germany), Borsigstrasse 23. German. Direktor des anorganisch chemischen Instituts der technischen Hochschule. Dr.phil. (Berlin, Universit.); Dr.Ing.ehrenheilber (Dresden, technissche Hochschule). Berichte der Deutschen Chem. Ges.; Zeits. f. Anorgan. Chemie, Elektrochemie, Angewandte Chemie, Colloidchemie. (*Signed by*) E. F. Armstrong.

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—— —— Paper No. 3. Coal dust explosions, Eskmeals, 1923 : a descriptive account. By RICHARD VERNON WHEELER. London 1924. pp. 29. ill.

—— —— Paper No. 4. First report of the Explosives in Mines Research Committee, 1922—1923. London 1924. pp. 12.

—— —— Paper No. 5. Flame-proof electrical apparatus for use in coal mines. First report—flange protection. By IRA CECIL FRANK STATHAM and RICHARD VERNON WHEELER. London 1924. pp. 50. ill.

—— —— Paper No. 6. The support of underground workings in the South Wales coalfield. (A report of the Support of Workings in Mines Committee.) London 1925. pp. 15.

—— —— Paper No. 35. Flame-proof electrical apparatus for use in coal mines. Third report—ring-relief protection. By H. RAINFORD and RICHARD VERNON WHEELER. London 1927. pp. 21. ill.

—— —— Paper No. 36. The ignition of gases by hot wires. By W. C. F. SHEPHERD and RICHARD VERNON WHEELER. London 1927. pp. 26. ill.

PENFOLD, ARTHUR RAMON. Tung oil (Chinese wood oil) from Australian grown trees of *Aleurites Fordii* (Hemsley). (*Sydney Technological Museum Bulletin No.* 12.) Sydney 1926. pp. 9.

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Building Research.* Special Report No. 8. Fire-resistant construction. By REGINALD EDWARD STRADLING and FRANK LAWRENCE BRADY. London 1927. pp. vi + 57. ill.

—— *Chemistry Research.* Special Report No. 1. The production of formaldehyde by oxidation of hydrocarbons. By WILFRID LEDBURY and ETHELBERT WILLIAM BLAIR. London 1927. pp. iv + 54. ill.

—— *Engineering Research.* Special Report No. 2. Properties of materials at high temperatures. II. Mechanical properties of 0·51 per cent. carbon steel, and 0·53 per cent. carbon cast steel. By H. J. TAPSELL and W. J. CLENSHAW. London 1927. pp. iv + 16. ill.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Lecture held at Burlington House on Thursday, November 24th, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

Professor W. A. Bone, F.R.S., delivered his Lecture, entitled "Gaseous Combustion at High Pressures." A vote of thanks to the Lecturer, proposed by Sir Robert Robertson, K.B.E., F.R.S., and seconded by Professor J. F. Thorpe, C.B.E., F.R.S., was carried with acclamation, Professor Bone making acknowledgment.

Ordinary Scientific Meeting, Thursday, December 1st, 1927, at 8 p.m., Professor H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death on September 9th, of Hermann Kast, who was elected a Fellow on December 2nd, 1926.

It was announced that it had been arranged for Fellows of the Society to obtain the publications of the Dutch Chemical Society at the following reduced rates:

"Chemisch Weekblad" .	Dutch Fl. 10 per annum (Regular price, Dutch Fl. 15).
"Recueil des travaux chimique des Pays-Bas"	Dutch Fl. 11.50 per annum (Regular price, Dutch Fl. 16.50).

Application should be made by Fellows direct to Dr. A. D. Donk, Secretary, Nederlandsche Chemische Vereeniging, Verspronckweg 100, Haarlem, Holland.

C. Chilvers was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

Basil Butterworth, B.Sc., 6, Belgrave Road, Wanstead, E. 11.
Jessie Cattermole, 207, Norbury Crescent, S.W. 16.
Moses Leverock Crossley, 734, Park Avenue, Plainfield, N.J., U.S.A.

Edgar Beattie Grant, 7, Alexandra Place, Jesmond, Newcastle-on-Tyne.
Thomas Hagyard, B.Sc., 3, Station Road, Eaglescliffe S.O., co Durham.
Miriam Ivy Horton, 59, Ingleby Road, Ilford.
Lilian Gertrude Thomerson, B.Sc., 134, Colchester Road, Leyton, E. 10.
Vera Millicent Thorn, B.Sc., 37, Steade Road, Sheffield.
Gladys Irene Sharp, 34, Woodhouse Road, Leytonstone, E. 11.
Richard Whittam, 120, Walmersley Road, Bury.

Dr. P. C. Austin and Dr. H. Hunter were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected:

Stanley Birks, M.A.
George Edward Kevin Blythe, B.Sc., Ph.D.
Charles Nightingale Clay, B.Sc., A.I.C.
William Ernest Cooper.
Philip Dalton Coppock, B.Sc., M.Sc.Tech.
Benjamin John Corder, B.A.
Eustace Nevill Eccott, B.Sc., A.R.C.S.
Herbert England.
Stephen de Finaly.
Robert Railton Fitzgerald.
Horace Leonard Gerry.
Thomas Joseph Glover, M.Sc., Ph.D.
Charles Robert Harington, M.A., Ph.D.
Edgar Albert Hayman.
Herbert Richard Hussey.
Albert William Kemp Ingram, B.A.
John William Thomas Jones, A.R.C.S.
Robert Napier Kerr, B.Sc., Ph.D.
Reginald Benjamin King, B.Sc., A.I.C.
Zenjiro Kitasato, D.Sc.
Frederick Goronwy Kny-Jones, B.Sc.
Cyril Dunn Lawrence, B.Sc.
Paul Nicholas Leech, A.B., Sc.M., Ph.D.
Barnett Levin, B.Sc.
Ronald Henry Linsell, B.Sc.
John McBride.
James Younger Macdonald, B.A.
James Eric McNeil, B.Sc.
Moolraj Mehrotra, M.Sc.
David Owen Meredith.
Arthur Hereward Millard.
Thomas Mitchell, B.Sc., A.R.C.S.
Shinzo Murakami.
Ryuzaburo Nodzu, D.Sc.
Mariam Puthenparampil Oommen, B.A.
William Alexander Hugh Oswald, B.A.
Harry Pavion.
Gordon Perrins.
Mata Prasad, D.Sc.
William Emrys Pride, B.Sc., A.R.C.S.
Bijoor Sanjiva Rao, B.A.
Walter Desmond Raymond.
David Clarence Rhys-Jones, B.Sc.
Albert Ernest Robinson.
Otto Ruff, Dr.Phil., Dr.Ing.Eh.
Ralph David Satchell, B.Sc., A.R.C.S.
William Dallas Scott, A.R.C.S.
Ian Campbell Somerville, B.Sc., Ph.D.
Arthur Harold Stevens, B.Sc.
Horatio Todd.
Robert Walton.
Frank Louis Warren, B.Sc., A.R.C.S.
Marjorie Jennet Wilson-Smith, B.Sc.

The following papers were read:

"Action of Beckmann's chromic acid mixture on some monocyclic terpenes." By T. A. Henry and H. Paget.

"The condensation of glyoxalines with formaldehyde." By R. Grindley and F. L. Pyman.

"Glyoxaline-4(5)-formaldehyde." By W. Hubball and F. L. Pyman.

"Studies of dynamic isomerism. Part XXVI. Consecutive changes in the mutarotation of galactose." By G. F. SMITH and T. M. LOWRY.

"Triazole compounds. Part II. Methylation of some 1-hydroxy-1 : 2 : 3-benztriazoles." By O. L. BRADY and C. V. REYNOLDS.

"The reaction between diaryloxy*iso*propyl alcohols and phosphorus oxychloride in the presence of pyridine." By D. R. BOYD and D. E. LADHAMS.

The Council has made the following Grants from the Research Fund:

	£	*s.*	*d.*
Constitution of iridin and irigenin. W. Baker. (Oxford Univ.)	7	0	0
The chemistry of Balbiano's acid. J. C. Bardhan (Imperial Coll.)	9	0	0
Constitution of columbin. W. Blakey. (Cambridge Univ.) ...	4	0	0
Organic compounds of arsenic. A. Brewin. (E. London Coll.)	7	0	0
Synthetical experiments in connexion with the alkaloids and related substances. R. K. Callow. (Oxford Univ) ...	7	0	0
Constitution of the disaccharides. W. Charlton. (Birmingham Univ.)	7	0	0
Catalytic effects produced by acids and salts (*contd.*). H. M. Dawson. (Leeds Univ.)	9	0	0
Determination of oxygen content in wrought iron and steel. C. H. Desch and H. H. Rains. (Sheffield Univ.)	9	0	0
Tautomerism of ketones of the type *cyclo*hexanylacetone (*contd.*). A. H. Dickins. (Imperial Coll.)	7	0	0
Three-carbon tautomerism. E. N. Eccott. (Imperial Coll.) ...	7	0	0
(*a*) Synthesis of *iso*indole. (*b*) Fission of sulphones with alkalis. G. W. Fenton. (Leeds Univ.)	14	0	0
Constitution of morphine. J. D. Fulton. (Manchester Univ.)...	7	0	0
Quasi-aromatic structures (*contd.*). F. R. Goss. (Leeds Univ.)	14	0	0
Relative directive powers of the halogens. L. G. Groves. (E. London Coll.)	4	0	0
Relative effects of the *meta*-orienting groups. H. C. Gull. (E. London Coll.)	4	0	0
Experiments on alkaloids and related substances. J. M. Gulland. (Oxford Univ.)	7	0	0
Properties of ω-bromoquinaldines, etc. D. L. Hammick. (Oxford Univ.	7	0	0
Constitution of carbohydrates. H. A. Hampton. (Birmingham Univ.)	7	0	0
Study of electrolytes in non-aqueous solutions. F. S. Hawkins. (E. London Coll.)	9	0	0
Influence of the solvent on reaction velocity in its bearing on the quantum theory. F. W. Hodges. (Chelsea Polytechnic)...	4	0	0
Reaction products of benzoyl chloride and benzoic anhydride with indigo. E. Hope. (Oxford Univ.)	7	0	0
Studies in azo- and azoxy-compounds. Miss M. I. Horton. (E. London Coll.)	4	0	0

	£	s.	d.
Three-carbon tautomerism in unsaturated nitriles. A. Kandiah. (Imperial Coll.)	7	0	0
Solvent effect on velocity of reaction. R. N. Kerr. (Bedford Coll.)	9	0	0
Properties of conjugated compounds. C. D. Lawrence. (Imperial Coll.)	7	0	0
Constitution of carbohydrates. A. Learner. (Birmingham Univ.)	7	0	0
Re-examination of certain large ring compounds. R. J. W. Le Fèvre. (Univ. Coll., London)	4	0	0
Synthesis and properties of symmetrically substituted diaryl hydrocarbons. A. W. Leonard. (E. London Coll.) ...	4	0	0
Effect of substituents on the formation of coumarin derivatives. A. B. E. Lovett. (E. London Coll.)	4	0	0
Synthesis of the compounds produced by the condensation of fluorene with acetone. P. Maitland. (Glasgow Univ.) ...	4	0	0
Competitive substitution effects in the benzene nucleus. H. A. Mayes. (E. London Coll.)	7	0	0
Comparison of thallium and dialkyl thallium salts with each other and with salts of the alkali metals. R. C. Menzies. (Bristol Univ.)	14	0	0
Three-carbon tautomerism. T. Mitchell. (Imperial Coll.) ...	7	0	0
Structure of carbohydrates. T. H. Morton. (Birmingham) ...	7	0	0
Stereoisomerism in polycyclic systems. S. G. P. Plant. (Oxford Univ.)	11	0	0
Heat of adsorption of oxygen on charcoal. E. K. Rideal and A. F. H. Ward. (Cambridge Univ.)	9	0	0
Condensation reactions of γ-diketones. E. Roberts. (E. London Coll.)	4	0	0
Syntheses of certain glucosides, and derivatives of certain hydroxy-acids. A. Robertson. (Manchester Univ.) ...	19	0	0
Mobility of three-carbon tautomeric systems. E. Rothstein. (Leeds Univ.)	19	0	0
Equilibrium mixtures of unsaturated methyl ketones. R. D. Satchell. (Imperial Coll.)	7	0	0
Properties of cyclic unsaturated acids. W. D. Scott. (Imperial Coll.)	7	0	0
Nitration of ethylbenzene and related substances. E. A. Seeley. (Derby Tech. Coll.)	7	0	0
Depression of orienting influences by substitution. Miss G. I. Sharp. (E. London Coll.)	4	0	0
Comparative velocities of nitration of ω-substituted toluenes. Miss F. R. Shaw. (Leeds Univ.)	7	0	0
Reactivity of halogens in halogenated derivatives of naphthalene. J. B. Shoesmith. (Edinburgh Univ.)	7	0	0
Oxide-ring structure of sugars. J. A. B. Smith. (Birmingham Univ.)	7	0	0
Singlet linkages in co-ordination and molecular compounds. S. Sugden. (Birkbeck Coll.)	9	0	0
Asymmetric organo-metallic derivatives. Miss L. G. Thomerson. (E. London Coll.)	4	0	0
Preparation of mono-substituted derivatives of piperazine, etc. Miss V. M. Thorn. (Sheffield Univ.)	4	0	0

	£	s.	d.
Conversion of aromatic amines into quinolines. E. E. Turner. (E. London Coll.)...	4	0	0
Nitration of *meta*-dihalogenobenzenes. C. C. N. Vass. (Leeds Univ.)	7	0	0
Synthetical experiments on the constitution of alkaloids. C. J. Virden. (Oxford Univ.)	7	0	0
Formation of large-membered rings. I. Vogel. (Imperial Coll.)	9	0	0
Chemistry of molybdenum and allied elements. W. Wardlaw. (Birmingham Univ.)	9	0	0
Investigations of sterols from *Arnica* root and from *Ononia spinosa* root. W. A. Waters. (Cambridge Univ.)	7	0	0
Bromination of acetyl bromide. H. B. Watson. (Univ. Coll., Bangor)	4	0	0
Constitution of carbohydrates. J. I. Webb. (Birmingham Univ.)	7	0	0
Laws governing substitution in the hydrazine molecule. J. Wilson. (Regent St. Polytech.)	4	0	0
Effect of *gem*-dialkyl groups on the formation and stability of the anhydrides of dicarboxylic acids. Miss M. J. Wilson-Smith. (Imperial Coll.)	9	0	0
	£434	0	0

List of Papers, or Abstracts thereof, received between November 17th and December 1st, 1927. This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.

"Nor-*d*-ψ-ephedrine, an alkaloid from *Ephedra* species." By S. SMITH.

"The alkaline hydrolysis of the nitro-ω-bromostyrenes and the nitro-ω-chlorostyrenes." By A. T. DANN, A. HOWARD, and W. DAVIES.

"The bromination of *m*-methoxycinnamic acid." By H. DAVIES and W. DAVIES.

"On Haber's glass cell." By W. S. HUGHES.

"The resolution of externally compensated *p*-nitrobenzoylalanine." By W. M. COLLES and C. S. GIBSON.

"Studies in adjacent substitution. Part I. Some reactions of 3-chloro-2-aminoanisole." By H. H. HODGSON and A. KERSHAW.

"The stereochemistry of reduced quinoxalines. Part III. The resolution of externally compensated α- and β-2 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines." By C. S. GIBSON, J. H. NUTLAND, and J. L. SIMONSEN.

"Studies in halogen compounds. Part I. The mechanism of activation of halogen atoms by the nitro-group. The relative reactivities of halogen atoms present in aromatic compounds." By A. BREWIN and E. E. TURNER.

"The migration of the acyl group in partially acylated phenolic compounds. Part II." By A. G. PERKIN and R. C. STOREY.

"The condensation of hexahydrobenzaldehyde and malonic acid." By S. S. G. SIRCAR.

"The salting-out effect. Influence of electrolytes on the solubility of *m*-cresol in water." By J. S. CARTER and R. K. HARDY.

"The cyanine dyes. Part X. The constitution of the *apo*-cyanines." By W. H. MILLS and H. G. ORDISH.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY

Fellows are reminded that application for the Annual Reports for 1927, Vol. XXIV, at 5*s*. 6*d*. per copy should be received by Mr. S. E. Carr without delay. Applications must be accompanied by a remittance for 5*s*. 6*d*.

ADDITIONS TO THE LIBRARY

I. *Donations.*

ABDERHALDEN, EMIL. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I. Chemische Methoden, Teil 11, Heft iii. Berlin 1927. pp. 217 to 632. ill. *M*. 22. (*Recd*. 7/12/27.)
From the Publishers: Herren Urban & Schwarzenberg.

BERTHOUD, ALFRED. Photochimie. Paris 1928. pp. viii + 324. ill. 40 *fr*. net. (*Recd*. 7/12/27).
From the Publishers: MM. G. Doin et Cie.

BRITISH ASSOCIATION OF CHEMISTS. The Chemical Practitioner. Vol. I, etc. London 1927 +. (*Reference*.) From the Association.

CHEMICAL SOCIETY OF JAPAN. Bulletin. Vol. I, etc. Tokyo 1926 +. (*Reference*.) From the Society.

[MINES DEPARTMENT.] *Safety in Mines Research Board*. Catalogue of books, pamphlets, abstracts, translations, etc., in the Library. [Sheffield] 1927. pp. 103. [In mimeograph form.] (*Reference*.) From the Department.

II. *By Purchase.*

HALE-WHITE, SIR WILLIAM. Materia medica, pharmacy, pharmacology, and therapeutics. 19th edition. London 1927. pp. viii + 712. 10*s*. 6*d*. net. (*Recd*. 22/11/27.)

HENDERSON, YANDELL, and HAGGARD, HOWARD W. Noxious gases and the principles of respiration influencing their action. New York 1927. pp. 220. ill. 19*s*. net. (*Recd*. 26/11/27.)

HOLLEMAN, ARNOLD FREDERIK. A text-book of inorganic chemistry. Issued in English in co-operation with HERMON CHARLES COOPER. 7th English edition. New York, 1927. pp. x + 542. ill. 37*s*. 6*d*. net. (*Recd.* 24/11/27.)

JELLINEK, KARL. Lehrbuch der physikalischen Chemie. 2nd edition. Vol. I, etc. Stuttgart 1927 +.

KENT-JONES, DOUGLAS WILLIAM. Modern cereal chemistry. Revised [2nd] edition. Liverpool 1927. pp. viii + 446. ill. 25*s*. net. (*Recd.* 22/11/27.)

KLEMGARD, E. N. Lubricating greases : a book of practical and scientific data on the manufacture and use of lubricating greases. New York 1927. pp. 198. 23*s*. net. (*Recd.* 26/11/27.)

LAURY, N. A. Hydrochloric acid and sodium sulfate. New York 1927. pp. 127. ill. 17*s*. net. (*Recd.* 26/11/27.)

LOEB, LEONARD B. Kinetic theory of gases. . . . Classical deductions with recent experimental advances. New York 1927. pp. xvi + 556. ill. 27*s*. 6*d*. (*Recd.* 26/11/27.)

OSTWALD, WOLFGANG. Die Welt der vernachlässigten Dimensionen. Eine Einführung in die Kolloidchemie. 9th and 10th edition. Dresden 1927. pp. xvi + 325. ill. *M*. 12. (*Recd.* 29/11/27.)

PARSONS, THOMAS RICHARD. Fundamentals of biochemistry in relation to human physiology. 3rd edition. Cambridge 1927. pp. xii + 308. ill. 10*s*. 6*d*. net. (*Recd.* 22/11/27.)

III. *Pamphlets.*

ADAMS, WILLIAM GRYLLS. On Grove's, Planté's, and Faure's secondary batteries. London 1881. pp. 14.

AERONAUTICAL RESEARCH COMMITTEE. Reports and Memoranda, No. 1079. Summary by the Secretary Engine Sub-Committee of a "Report on anti-knock investigations." By ALFRED [CHARLES GLYN] EGERTON and S. F. GATES. London 1926. pp. 13. ill.

BURTON, WILLIAM KINNINMOND. The refraction of light and lenses. London 1882. pp. [11]. ill.

CATHCART, C. H. The phenomena of phosphorescence and fluorescence. London 1882. pp. [10].

JOHNSON, GEORGE STILLINGFLEET. Chemical and molecular stability. London 1882. pp. [5].

—— On the absence of sugar from normal human urine. (From the *Med.-Chir. Trans.*, 1894, 76.)

KOGERMAN, PAUL NICOLAI. The chemical nature of Estonian oil-shale. The origin of oil-shales. (From the *Sitz. Nat.-Ges. Univ. Tartu*, 1927, 34, (2).)

NEW SOUTH WALES. *Legislative Assembly.* Report of the

Director-General of Public Health for the year ended 31st December, 1925. Section I.–C. Industrial hygiene. Section IV. Sixteenth Report of the Microbiological Laboratory. Sydney 1927. pp. [46], [45]. ill.

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Forest Products Research.* Special Report No. 1. The air-seasoning and conditioning of timber. By F. M. OLIPHANT. London 1927. pp. vi + 26. ill.

—— *Fuel Research.* Fuel for motor transport: fourth memorandum. Power alcohol from grasses, straws, and waste vegetable materials. London 1927. pp. vi + 26.

—— —— Physical and chemical survey of the national coal resources, No. 9. The Lancashire coalfield: the Ravine seam. Part ii. Carbonisation in continuous vertical retorts. London 1927. pp. vi + 37. ill.

SODEAU, WILLIAM HORACE. The decomposition of chlorates, alone and in presence of other substances. London 1898. pp. 48.

SODEAU, WILLIAM HORACE, and GIBSON, CHARLES STANLEY. The use of plaster of Paris as an impression material. (From the *British Dental J.*, 1927.) ill.

STAPLETON, HENRY ERNEST, AZO, R. F., and HUSAIN, M. HIDĀYAT. Chemistry in 'Irāq and Persia in the tenth century A.D. (From the *Mem. Asiatic Soc. Bengal*, 1927, 8.)

SULLIVAN, MICHAEL XAVIER. A distinctive test for cysteine. (From the *U.S. Public Health Reports*, 1926, **41**.)

THOMSON, JOHN MILLAR. On the action of light upon certain substances and its application to photography. London 1882. pp. [10].

UNITED STATES. *Department of Agriculture.* Department Circular 419. Grouping of soils on the basis of mechanical analysis. By R. O. E. DAVIS and H. H. BENNETT. Washington 1927. pp. 14.

—— *Department of Commerce.* Bureau of Standards. Circular No. 33. [4th edition.] United States Government master specification for cement, Portland. Washington 1927. pp. 18. ill.

—— —— —— United States Government master specification for cement, plastic magnesia (magnesia–oxychloride) used as flooring, bases, wainscots, etc. Washington 1927. pp. 16. ill.

—— —— —— Scientific Paper No. 551. Absorption spectra of iron, cobalt, and nickel. By W. F. MEGGERS and F. M. WALTERS, *jun.* Washington 1927. ill.

—— —— —— Scientific Paper No. 557. A suggested new base point on the thermometric scale and the $\alpha \rightleftharpoons \beta$ inversion of quartz. By FREDERICK BATES and FRANCIS P. PHELPS. Washington 1927. ill.

ADDITIONS TO THE LIBRARY OF THE CHEMICAL SOCIETY DURING THE YEAR 1926.

ABDERHALDEN, EMIL. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I. Chemische Methoden, Teil 1, Heft iv. Abt. III. Physikalisch-chemische Methoden, Teil B, Heft iii. Berlin 1926. Abt. XI. Methoden zur Erforschung der Leistungen des Pflanzenorganismus, Teil 3, Heft iv. Berlin 1925–6.

ACCUM, FREDRICK. *See* BROWNE, CHARLES ALBERT.

ADIE, RICHARD HALIBURTON. Chemistry for agricultural students. London 1926. pp. viii + 358. ill.

AGRICOLA, GEORG. *See* DARMSTAEDTER, ERNST.

ALEXANDER, JEROME. [Editor.] Colloid chemistry, theoretical and applied. By selected international contributors. Vol. I. Theory and methods. New York 1926. pp. 974. ill.

ALLEN, PAUL W. Industrial fermentations. New York 1926. pp. 424. ill.

ALLIOTT, EUSTACE ALEXANDER. Centrifugal dryers and separators. London 1926. pp. 152. ill.

ALSBERG, CARL LUCAS, and GRIFFING, E. P. Effects of fine grinding upon flour. (From *Cereal Chemistry*, 1925, 2.)

AMERICAN BAKER'S ASSOCIATION. [later] AMERICAN INSTITUTE OF BAKING. Baking Technology: a journal of applied science in baking. Vol. I, etc. Chicago 1922 +. (*Reference.*)

AMERICAN INSTITUTE OF BAKING. *See* AMERICAN BAKER'S ASSOCIATION.

AMERICAN MEDICAL ASSOCIATION. Archives of Internal Medicine. Vol. 37, etc. Chicago 1926 +. (*Reference.*)

AMERICAN PETROLEUM INSTITUTE. *See* UNITED STATES. *Department of the Interior.*

ARCHIVES OF INTERNAL MEDICINE. *See* AMERICAN MEDICAL ASSOCIATION.

ARNALL, FRANCIS. *See* COLEMAN, JOSEPH BERNARD.

ARNALL, FRANCIS, and HODGES, FRANCIS WILLIAM. Theoretical organic chemistry. Part I. London 1926. pp. xii + 372.

ARRHENIUS, SVANTE AUGUST. Chemistry in modern life. Translated from the Swedish by CLIFFORD SHATTUCK LEONARD. London 1926. pp. xvi + 286. ill.

ASLIN, MARY S. *See* ROTHAMSTED EXPERIMENTAL STATION LIBRARY.

ASSOCIAZIONE ITALIANA DI CHIMICA GENERALE ED APPLICATA. Stanislao Cannizzaro: scritti vari e lettere inedite nel centenario della nascita. Roma 1926. pp. viii + 486. ill.

ATACK, FREDERICK WILLIAM. [Editor.] The Chemists' Year Book 1926. Manchester [1926]. pp. xii + 1198. ill. (*Reference.*)

AUB, JOSEPH C. [and others]. Lead poisoning. With a chapter on the prevalence of industrial lead poisoning in the United States by ALICE HAMILTON. Baltimore 1926. pp. x + 266. ill.

AUSTRALIA, COMMONWEALTH OF. *Department of Defence.* The laboratories of the Munitions Supply Board. Melbourne 1926. pp. 7. ill.

AUSTRALIAN CHEMICAL INSTITUTE. 8th Annual Report. 1924–1925. Sydney 1925. pp. 82.

AUSTRALIAN NATIONAL RESEARCH COUNCIL. *See* PAN-PACIFIC SCIENCE CONGRESS.

BABLIK, HEINZ. Galvanizing: a theoretical and practical treatise. Translated by CHARLES T C. SALTER. London 1926. pp. viii + 168. ill.

BAILEY, CLYDE H. The chemistry of wheat flour. New York 1925. pp. 324. ill.

BAKING TECHNOLOGY. *See* AMERICAN BAKER'S ASSOCIATION.

BANCROFT, WILDER DWIGHT. Applied colloid chemistry: general theory. 2nd edition. New York 1926. pp. x + 490. ill.

BARR, GUY. *See* NERNST, WALTER.

BARTON, LARRY J. Refining metals electrically. Cleveland, Ohio 1926. pp. viii + 414. ill.

BATE, STANLEY CHARLES. The synthesis of benzene derivatives. London 1926. pp. 230.

BEACALL, THOMAS [and others]. Dyestuffs and coal tar products. 4th edition. London 1926. pp. xii + 168. ill.

BEAUMONT, ROBERTS. The finishing of textile fabrics (woollen, worsted, union and other cloths). 2nd edition. Revised by ALEX. YEWDALL. London 1926. pp. xvi + 368. ill.

BERICHTE DER DURSTIGEN CHEMISCHEN GESELLSCHAFT. Berlin 1886. pp. [iv. + 52]. (*Reference.*)

BEYERSDORFER, PAUL. Staub-explosionen. Dresden 1925. pp. viii + 125. ill.

BLASWEILER, TH. E. The use of sodium silicate for the sizing of paper. Translated from the German. London 1926. pp. xx + 114.

BLIGH, NEVILLE MELTON. The evolution and development of the quantum theory. London 1926. pp. 112. ill.

BOEHMER, NORRIS. *See* ELLIS, CARLETON.

BORN, MAX. Probleme der Atomdynamik. Berlin 1926. pp. viii + 184. ill.

BOWLES, THOMAS HENRY. *See* FOX, JOHN JACOB.

BRAUN, JULIUS VON. Lehrbuch der organischen Chemie. Leipzig 1925. pp. xii + 508.

BRIGGS, DENNIS BROOK. Classified problems in chemistry. London 1926. pp. viii + 152.

—— Practical glass manipulation. London 1926. pp. xvi + 39. ill.

BRITISH DRUG HOUSES. The B.D.H. book of A.R. standards. London 1926. pp. xiv + 112. (*Reference.*)

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